MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY
REMEDIATION AND REDEVELOPMENT

GENERAL GUIDANCE

FOR

EVALUATING AND CHARACTERIZING

PETROLEUM RELEASES

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RESCINDED

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NOTE: CHAPTER 10 IS THE ONLY CHAPTER THAT REMAINS IN EFFECT IN THIS DOCUMENT. For balance information, see RRD Operational Memorandum 2.

TABLES

RESCINDED

1.0 INTRODUCTION

Use of this guidance is intended for DEQ staff, owner/operators, and their consultants and contractors involved in the investigation and cleanup of petroleum hydrocarbon releases or the regulatory review of such releases under Part 213, Leaking Underground Storage Tanks (LUST), of the Natural Resources and Environmental Protection Act 1994 PA 451, as amended. The purpose of this guidance is to bring together information concerning the selection of appropriate parameters associated with measurement of various petroleum product releases, guidance for the use of field and laboratory measurements in the investigation of such releases, guidance for proper sample handling, and guidance for selection of cleanup limits. The Storage Tank Division (STD) has incorporated risk-based corrective action (RBCA) for both site characterization and remediation, and has adopted by reference American Society for Testing and Materials' (ASTM) "Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites" (E (E1739-95).

This guidance is not intended to convey any rights to any parties, nor create any duties or responsibilities under the law. This guidance and matters addressed herein are subject to revision. The effective date of this revision is <u>September 15, 1999</u>. This guidance applies to any petroleum hydrocarbon investigation initiated after the effective date of this guidance, or any petroleum hydrocarbon site with a corrective action plan dated after the effective date of this guidance.

RESCINDED

2.0 *PETROLEUM AND PETROLEUM PRODUCTS*

A basic understanding of the major components of petroleum products is necessary to properly select appropriate analytical methods for monitoring or measurement of various petroleum products and to follow them as they move, partition or degrade in the environment. The following section provides information concerning the major components of these products.

2.1 Petroleum Fractions

Petroleum is separated by distillation into various fractions. Because of the relationship between boiling point and molecular weight, this amounts to a rough separation according to carbon number. Each fraction is a complicated mixture containing a range of carbon numbers and molecular structures. The use that each fraction is put to depends on its volatility or viscosity. Examples of fractions separated by distillation are listed as follows.

Fraction	Dist. Temp. (°C)	Carbon Number/Main Constituents
Natural Gas	Below -88 °C	C_1-C_2
Liquefied Gas	Below 1 °C	C_3-C_4
Petroleum Ether	20 - 60 °C	C_5-C_6, cycloalkanes
Gasoline	40 - 205 °C	C_5-C_{10}, cycloalkanes
Napthas Stoddard Solvents Thinners	100 - 200 °C	C_5-C_{13}, cycloalkanes, and aromatics
Kerosenes	175 - 325 °C	C_{12}-C_{18}, and aromatics
Fuel Oils	275 - 345 °C	C_{12}-C_{20} and higher alkanes
Lubricating Oils	345 - 540 °C	C_{20}-C_{34} paraffinic and cycloparaffinic based oils
Asphaltic Residue	Above 540 °C	Bitumen or Asphaltenes (large polycyclic compounds)

2.2 Major Petroleum Products

2.2.1 Natural Gas

Natural gas contains the smaller and more volatile alkanes consisting mainly of methane and progressively smaller amounts of ethane, propane, isobutanes, butanes, isopentane, and n-pentane. Natural gas is used chiefly for heating. Propane and butane are liquefied in tanks and sold as Liquefied Petroleum (LP) Gas.

2.2.2 Petroleum Ether

Petroleum ether is composed mainly of C_5 and C_6 compounds including pentane, 2-methylpentane, 3-methylpentane, cyclopentane, 2,2-dimethylbenzene, 2,3-dimethylbutane and isopentane. Petroleum ether is used as a universal solvent and extractant for chemicals, fats, waxes, paints, varnishes, and furniture polishes.

2.2.3 Gasoline and Gasoline Additives

Gasoline is a variable and complex blend of distillation temperature fractions to meet a wide variety of engine designs and operating conditions. Gasoline is blended for the monthly temperature and altitude of the area where it is used. It is also made in different grades or octane ratings to meet the needs of different internal combustion engines. Gasoline differs between companies, refineries, and even between batches from the same refinery. Gasoline contains 11-25% C_3-C_{12} straight chain alkanes, 18-57% C_4-C_{10} branched alkanes, 0.7-2.6% C_5-C_8 cycloalkanes, 2.3-3.5% C_4-C_7 straight chain alkenes, 3.3-4.0% C_5-C_7 branched alkenes, 11-56% C_6-C_{12} alkylbenzenes, and 0.1 to 0.5% C_{10}-C_{12} polynuclear aromatic hydrocarbons.

Gasoline additives include various antiknock compounds, dyes, corrosion inhibitors, antioxidants, octane boosters, and icing inhibitors. Prior to 1996, tetraethyllead was the primary organolead additive to leaded gasoline and was permitted under EPA regulations up to 1,100 mg/l as lead, to increase octane ratings. Other organolead compounds used within the last 10 years include tetramethyllead, trimethyllead, dimethyllead, and methyltriethyllead. Organolead compounds in unleaded gasoline are restricted to 13 mg/l as lead. The use of organolead compounds in gasoline has been greatly reduced in recent years. The last producer of organolead additives in the United States stopped making them in early 1991. 1,2-dichloroethane (1,2-DCA) and Ethylene Dibromide (EDB) were added to leaded gasoline to keep organolead combustion products volatile for discharge with exhaust gases instead of being deposited in the engine combustion chamber. The amount of added 1,2-DCA or EDB is proportional to the amount of organolead.

Leaded aviation gasoline, because of its higher octane rating, will contain up to double the amount of lead and lead scavengers (1,2-DCA or EDB) contained in leaded automotive gasoline. In 1990, six percent of all gasoline produced in the U.S. was leaded gasoline. After December 31, 1995, use of leaded gasoline as a motor vehicle fuel was prohibited as per Section 211 of the Clean Air Act Amendments of 1990. Methanol, ethanol, tertiary-butyl-alcohol (TBA), methyl-tertiary-butyl-ether (MTBE), ethyl-tertiary-butyl-ether (ETBE), and tertiary-amyl-methyl-ether (TAME) are added as blending agents to increase octane ratings of unleaded gasoline. These oxygenated compounds may also be required in Clean Air Act carbon monoxide non-attainment areas to reduce carbon monoxide emissions. Toluene and xylene are also added as blending agents to increase octane ratings.

2.2.4 Stoddard Solvent and Other Petroleum Solvents

Stoddard Solvent, also called white spirits, is a mixture containing hydrocarbons from C_5 to C_{13} with the majority of hydrocarbons in the C_9-C_{11} range, and with a boiling point range of between 155-200 ^{0}C. There are several different formulations, but in general the hydrocarbons composing stoddard solvent are 30-50% alkanes, 30-40% cycloalkanes, and 10-20% aromatics. Specific compounds and amounts measured in some formulations and appearing on EPA regulatory lists, or listed in analytical methods include: acenaphthenes (0.4%), n-propylbenzene (2.0%), 1,2,4-trimethylbenzene (0.9%), naphthalene (0.2%), and acenaphthalenes (0.3%). Stoddard solvent is a multipurpose petroleum solvent. Industrial uses include paint vehicles; thinning agents for paints, coatings, and waxes; printing inks; adhesives; as a solvent in liquid photocopier toners; and as a degreaser in machine and automotive repair shops.

Other petroleum solvents include petroleum spirits, mineral spirits, varnish maker's and painter's (VM&P) naphthas. These products are general-purpose thinners and solvents for paint and varnish. The chemical composition is similar to stoddard solvent, but the range of boiling points in this category of products is broader.

2.2.5 Kerosene and Jet Fuels

Kerosene is used in heating and as an aviation turbine fuel (Jet A and B). Kerosene for heating purposes is available as a special low sulfur grade for use in non-flue connected kerosene burner appliances, and as a regular grade for use in flue connected burner appliances.

Jet fuels are made by blending and refining crude oil petroleum products such as naphtha, gasoline, or kerosene to meet specific military or commercial specifications. JP-4 and JP-7 are military specifications; Jet A and Jet A-1 are commercial or civilian specifications.

JP-4 is intended for use in advanced supersonic aircraft and is a naphtha-type fuel made by blending straight-run kerosene streams and lower boiling streams to fit the composition containing approximately (by weight) 43% C_4-C_{14} alkanes, 11% C_6-C_{10} cycloalkanes, 12% C_6-C_{10} alkylbenzenes, and 2% C_{10}-C_{12} naphthalenes. It is known as a wide-cut fuel made from distillation products obtained over a wide range of temperatures, and has a broad spectrum of individual compounds with chain lengths ranging from C_4-C_{16}.

JP-7 is made by blending kerosene distillates to achieve a product containing a maximum of 5% aromatics by volume and a maximum of 0.1% sulfur by weight. One example of JP-7 contained approximately (by volume) 97.4% C_{10}-C_{17} alkanes, 0.4% C_{10}-C_{11} cycloalkanes, 1.6% C_{10}-C_{12} alkylbenzenes, and 0.6% C_{10}-C_{11} naphthalenes.

Jet A and Jet A-1 are kerosene type fuels, used in commercial jet aircraft. Jet A-1 is similar to Jet A, except that the freezing point is lower for long duration international flights. Jet A-1 is the military equivalent of JP-8.

2.2.6 Fuel Oils

Fuel oils are classified as distillates or residuals based on production methods. The distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from distillation. Grades No. 1 and 2 are distillates, and grades No. 4 to 6 are usually residuals (Grade No. 3 is no longer produced). Grade No. 1 is a light distillate, consisting of hydrocarbons in the C_9-C_{16} range, and intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue. Grade No. 2 is a heavier distillate, usually blended, consisting of hydrocarbons in the C_{11}-C_{20} range, and intended for use in atomizing type burners, which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade is used in most domestic burners and in many medium capacity commercial-industrial burners. Grade numbers 4, 5, and 6 (Bunker C) are progressively heavier residuals intended for burners designed to handle their associated viscosity ranges. In the heavier residuals, preheating may be necessary to atomize the fuel or pump the fuel from the storage tank.

The individual PNA compounds and levels present in fuel oil grades are variable. For comparison, PNAs present in fuel oil No. 1 include naphthalenes (2.8%) and acenaphthenes (0.4%); PNAs present in No. 2 fuel oil include naphthalenes (8.2%), acenaphthenes (2.6%), fluorenes and acenaphthylenes (1.4%), and phenanthrenes (1.4%).

2.2.7 Diesel Fuels

Diesel fuels contain predominantly a mixture of C_{10}-C_{19} hydrocarbons and are available in three grades based on volatility, ignition quality, viscosity, and other characteristics. Grade No. 1-D comprises the class of volatile fuel oils from kerosene to intermediate distillates. Fuels within this grade are applicable for use in high-speed engines in services involving frequent and relatively wide variations in loads and speeds as well as abnormally low temperatures. Grade No. 2-D includes the class of distillate gas oils of lower volatility. These fuels are applicable for use in high-speed engines in services involving relatively high loads and uniform speeds or engines not requiring high volatility or properties of Grade No. 1-D. Grade No. 4-D covers the class of more viscous distillates and blends of these distillates with residual fuel oils. These fuel oils are applicable for use in low and medium speed engines employed in services involving sustained loads at substantially constant speed. Octyl nitrate is added to some diesel fuels as an ignition improver (as measured by cetane number) at 0.1% to 0.2% by volume.

2.2.8 Hydraulic Fluids

Hydraulic fluids are a very diverse group of products and include automatic transmission fluid, brake fluid, shock absorber fluid, power steering fluid, floor hoist and hydraulic jack fluids, as well as fluids for various hydraulic machinery, earth moving equipment, high-lows, and other heavy industrial and construction equipment. This group also includes industrial cutting oils and cooling oils. Hydraulic fluids are of three types: 1) Mineral oil based fluids which make up over 90% of all hydraulic fluids; 2) Fire-resistant hydraulic fluids which are of four types: high water-based (99-96% water), water-in-oil emulsions (mineral oil based, 40% water), water-glycol solutions (35% water), and water-free pure chemical fluids of which phosphate esters are the most common; and 3) Synthetic fluids of four main types: synthesized hydrocarbons (composed of olefin oligomers, alkalated aromatics, polybutenes, and cycloaliphatics), organic esters, polyglycols, and phosphate esters.

2.2.9 Lubricating Oils

Lubricating oils contain predominantly a mixture of C_{20}-C_{34} hydrocarbons. They are made from the more viscous portion of the crude oil which remains after removal of gas oil and lighter fractions by distillation. Many petroleum derived hydraulic oils are similar, but are discussed separately as hydraulic fluids. These generally range from low viscosity oils with molecular weights as low as 250 to very viscous lubricants with molecular weights as high as 1000. The types of hydrocarbon compounds present in lubricating oils include normal (n-), and iso- alkanes, cycloalkanes, aromatics, and mixed alkane, cycloalkane, and aromatic ring compounds. These include SAE viscosity engine oil grades 5W through 50 and gear, axle, and manual transmission lubricant grades 75W through 250.

To minimize variation and produce lubricating oils that provide consistent performance, crude oils are selected and segregated according to principal type. The oil is distilled to achieve the appropriate boiling point range; undesirable constituents are removed; and oils are blended with other oils to attain the appropriate physical characteristics. Crude oil stocks are categorized as paraffinic and cycloparaffinic. Cycloparaffinic crude oil contains no wax, has a low pour point (-46°C), and is most desirable for the range of temperatures in automotive engines. Paraffinic stock requires dewaxing to reduce its pour point from approximately 27 to -18°C, and is less desirable for use in automotive engines. Lubricating oils may contain up to 30% additives inclu provers, defoamers, oxidation inhibitors, antiwear con RESCINDED discussion of the various refining processes; cracking, upg lube oil additives necessary to yield the final product is beyond the scope of this guidance.

2.2.10 Asphalts and Tars

Asphalt and tar building materials include binders for asphalt concrete, hot road surface oils, joint fillers, roofing tars and asphalts, dust laying oils, water proofing tars for building foundations, and similar products.

3.0 FATE AND TRANSPORT

An understanding of the fate and transport mechanisms and contaminant pathways associated with contaminant releases to the environment is necessary to develop a monitoring program, or collect the necessary information leading to remedial action. This is particularly true in the case of petroleum and its products since they are complex mixtures of many different components and additives. These components have different chemical and physical characteristics which control their behavior in releases to soil and water.

Persistence of organic compounds depends on several environmental factors, including soil organic matter, total precipitation and intensity, temperature, sunlight, and soil texture. Organic chemicals in soil are subject to one or more of seven possible fates: adsorption, volatilization, microbial degradation, photodecomposition, translocation to plants, chemical degradation, and leaching to groundwater. In the case of petroleum products released from underground tanks, adsorption, microbial degradation, and leaching to groundwater are usually very important; volatilization and chemical degradation are generally less important; and photodecomposition and plant uptake are usually unimportant.

The persistence and fate of organic compounds in soil depends on temperature, moisture, and soil texture. The greater the temperature, the greater the volatility, the more active the microbial population, the more rapidly concentrations of organic contaminants will be reduced. Soil moisture affects microbial activity. Microbial activity is reduced if a soil is either too wet or too dry. Volatility is also affected by moisture content; the nature of the effect depends on the solubility of the chemical. The total amount, intensity, and frequency of rainfall affect movement of chemicals in soil. The amount of soil organic matter (organic carbon content) is directly influenced by the soil texture. Coarse sandy soils will normally contain little organic matter. Therefore, water percolation will be rapid and leaching potential of chemical compounds will be high regardless of octanol/water or octanol/carbon partition coefficients. The opposite is true for heavy (i.e., clayey) soils. Water solubility of organic contaminants has the greatest affect on persistence and mobility of organic chemicals. The higher the molecular weight, the lower the solubility, and the higher the degree of halogenation, the lower the water solubility.

Table 5 contains boiling points, water solubilities, and octanol/water partition coefficients for some common petroleum constituents and additives used for monitoring and regulating petroleum product losses. Boiling point can be used as an indication of the kind of petroleum products (based on product distillation temperature) the compounds may be found in. Water solubilities and octanol/water partition coefficients are relative indicators of a compound’s ability to partition into water. Benzene has an octanol/water partition coefficient of 135; meaning that if benzene were added to a mixture containing equal parts octanol and water, 135 parts of benzene would partition into the octanol and 1 part of benzene would partition into the water. In general, the lower the water solubility, the higher the octanol/water, and octanol/carbon partition coefficients.

3.1 Petroleum Hydrocarbons

Upon a release to the environment, the hydrocarbon components selectively partition to the atmosphere, soil, or water according to their physical and chemical properties. Gasoline, for example, can exist as a free moving liquid, adsorbed to soil particles, dissolved in groundwater, and as a vapor. When a hydrocarbon is released from an underground storage tank, it percolates down through the interconnected pores of the soil as a result of gravity, capillary effects, adsorption, and leaching with precipitation. Liquid gasoline, as a result of its lower than water viscosity, will move through the unsaturated zone 2-3 times faster than water. As it moves downward through the unsaturated zone, it also spreads laterally due to capillary effects and irregularly as a result of the heterogeneity in the soil. Product within the unsaturated zone is partitioned between the water, solid and the air components. The most water insoluble components tend to adsorb to the soil particles; water soluble components dissolve in the suspension water; and the volatile components partition to the pore spaces. The speed with which the product moves and the amount of product or product constituents that remain in the unsaturated zone or move to the groundwater depends on the amount of product released, the characteristics of the product, the characteristics of the soil, and other related factors. If the amount of product released is large relative to the depth of groundwater, soil retention capacity may be exceeded and bulk fluid transport to the groundwater may occur.

As the product enters the transitional zone between the saturated and unsaturated zones, known as the capillary zone, it migrates laterally. As it migrates, it can re-enter the unsaturated zone above the capillary zone by surface wetting or wicking. The wicking effect, plus vertical groundwater fluctuation, also affects the distribution of the product within the capillary zone. As the product reaches the groundwater, the soluble components partition into and migrate with groundwater, and the insoluble components float on the water surface as a “pancake” or lens shaped mass. In the case of gasoline, this floating layer migrates at slightly more than half the groundwater velocity. The heavier the product the slower the movement. The soluble components in the groundwater also experience a chromatographic effect which cause the more soluble components to travel at greater velocities than the less soluble components.

Gasoline will undergo “weathering” over time that will result in change in the relative concentrations of constituent hydrocarbons. In the case of BTEX compounds “weathering” results in reduction of the lighter, more soluble, more degradable BTEX compounds so that the relative concentration is shifted to heavier and more persistent BTEX compounds. Where soils are exposed to the atmosphere, low molecular weight hydrocarbons (such as C_5-C_9 alkanes and aromatics) are more likely to volatilize from soil surfaces, rather than be biodegraded. Reduction of higher molecular weight aliphatic and aromatic constituents will occur by both slow volatilization and by biodegradation. Biodegradation rates will be preferential, with the rate being fastest for low molecular weight aromatics and slower for aliphatic (alkanes, alkenes, dienes and alkynes) hydrocarbons that are branched or cyclic or that contain 10 or more carbons. Some hydrocarbons may not degrade.

Bacteria appear to be the most important microbes in the degradation of petroleum hydrocarbons in soil. Normal alkanes, normal alkylaromatics, and aromatics in the C_{10}-C_{12} range are the most readily degradable hydrocarbons. Normal alkanes, alkylaromatics, and aromatics above C_{22} are generally not available for metabolism by soil microbes because of their limited water solubility and solid physical state. Higher molecular weight hydrocarbons adsorbed to soil particles are generally unavailable for metabolism by microorganisms. Hydrocarbons in the C_5-C_9 range are biodegradable only at low concentrations since at higher concentrations they exhibit toxicity to soil microbes and are generally removed by volatilization. Polynuclear aromatic hydrocarbons (PNAs) and cycloalkanes are relatively resistant to biodegradation. The rate of biodegradation is highly dependent upon several site specific factors including temperature, oxygen content, moisture content, nutrient content, salinity, and pH.

PNAs can be placed in four general categories based on their octanol/water partition coefficients (K_{ow}) and tendencies to adsorb to soil. The naphthalenes with K_{ow} values near 2,000 have low adsorption capacity to soils relative to other PNAs. Acenaphthene, acenaphthylene, anthracene, fluorene, and phenanthrene have K_{ow} values in the range of 10,000 to 30,000 indicating a moderate potential to be adsorbed to soil. Fluoranthene and pyrene have K_{ow} values in the 80,000 range indicating a high potential for soil adsorption; and the high molecular weight compounds (benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene) have K_{ow} values in the range of 400,000 to 700,000, indicating a very high potential to adsorb to soil.

3.2 Metals

The fate of metals in soil is dependent on the characteristics of the individual metallic salts and other metallic compounds and complexes (especially solubility), the properties of the soil (pH, cation exchange capacity, texture, organic composition), and the characteristics of the leaching fluid (amount and pH). The relative retentions of metals in soil are in the order of lead > antimony > copper > chromium > zinc > nickel > cobalt > cadmium.

3.2.1 Lead and Tetraethyllead

The downward movement of lead from soil to groundwater by leaching is very slow under most natural conditions except for highly acidic situations. The conditions that induce leaching are: the presence of lead in soil at concentrations that either approach or exceed the cation exchange capacity of the soil; the presence of materials in soil that are capable of forming soluble chelates with lead; and a decrease in the pH of the leaching solution (e.g., acid rain). Leaching of soluble lead from contaminated soils into groundwater may be minimized by the presence of lead carbonate in the soil, and by maintaining a soil pH of 8-10.

Limited data indicate that tetraethyllead and tetramethyllead are converted to water soluble lead compounds in soil. Although tetraethyllead and tetramethyllead are not expected to leach significantly through soil, their highly water-soluble metabolites, trialkyl lead oxides, may be subject to leaching.

The concentration of lead in topsoil varies widely due to deposition and accumulation of atmospheric particulates from man-made sources. Levels of lead in the upper layer of soil (top six inches) along road sides may be 30-2,000 mg/kg higher than natural levels. These levels drop exponentially up to 25 meters from the roadway.

3.2.2 Cadmium

Phosphate fertilizers are a major source of cadmium input to agricultural soils. The natural cadmium concentration in phosphate fertilizers ranges from 3 to 100 mg/kg. Mean levels in uncontaminated topsoil in the United States are approximately 0.25 mg/kg. Topsoil levels are often more than twice as high as subsoil levels as a result of atmospheric fallout. Cadmium is also released through tire wear.

Cadmium is more mobile in aquatic environments than most other heavy metals. Cadmium concentration in water is inversely related to the pH and the concentration of organic material in the water. Important factors affecting transformation in soil include the cation exchange capacity, the pH, and the content of clay minerals, carbonate minerals, oxides, organic matter, and oxygen. Cadmium in soils may leach to water especially under acidic conditions.

3.2.3 Chromium

The important valence states of chromium are II, III, and VI. Elemental chromium (0) does not occur naturally. The divalent state is relatively unstable and is readily oxidized to the trivalent state (or chromic state). Chromium compounds are stable in the trivalent state and occur naturally in ores such as in ferrochromite. Hexavalent chromium (VI or chromate) is the second most stable state. However, hexavalent chromium is usually associated with man made sources and rarely occurs naturally.

Trivalent chromium compounds, with the exception of acetate, hexahydrate of chloride, and nitrate salts are generally insoluble in water. Some hexavalent chromium compounds, such as chromium (VI) oxide (or chromic acid), and the ammonium and alkali salts (e.g., calcium and strontium) of chromic acid are less soluble in water. The zinc and lead salts of chromic acid are practically insoluble in cold water. The hexavalent chromium compounds are reduced to the trivalent form in the presence of oxidizable organic matter. However, hexavalent chromium compounds are more stable in natural waters where there is a low concentration of reducing materials.

Chromium released into the environment from combustion of natural gas, oil and coal is present mainly as chromium (III) oxide. Dust from asbestos brake linings (asbestos may contain approximately 1,500 mg/kg of chromium), and emissions from chromium based catalytic converters are other sources of chromium associated with automobiles, but are minor in comparison to chromium from combustion of fossil fuels. Chromium in soil is mostly present as insoluble carbonate and chromium (III) oxide; and will therefore not be mobile in soil. The solubility of chromium in soil and its mobility may increase due to the formation of soluble complexes with soil organic matter. A lower soil pH may facilitate formation of soluble complexes.

The sorption of chromium to soil depends primarily on the clay content of the soil and to a lesser extent, on Fe_2O_3 and the organic content of soil. Chromium that is irreversibly adsorbed to soil, for example in the interstitial lattice of goethite, FeO (OH), is not leachable or otherwise available. Organic matter in soil is expected to convert soluble chromate, chromium (VI), to insoluble chromium (III) oxide, Cr_2O_3. Soluble and unabsorbed chromium (VI) and chromium (III) complexes in soil may leach into groundwater. The leachability of chromium (VI) in the soil increases as the pH of the soil increases. On the other hand, lower pH present in acid rain may facilitate leaching of acid soluble chromium (III) and chromium (VI) compounds in soil.

4.0 TARGET ANALYTES AND OTHER COMPOUNDS

4.1 Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX)

BTEX compounds are important for the investigation of gasoline releases to groundwater due to their abundance in gasoline (benzene (0.1-3.5%), toluene (2.7-21.8%), ethylbenzene (0.4-2.9%), and xylenes (3.2-8.5%)), the risk posed by these compounds, especially benzene, and the solubility of these compounds in groundwater. BTEX compounds are also useful for evaluating gasoline releases to soil. However, these compounds (especially benzene) tend to move into the aqueous phase more rapidly and are more susceptible to microbial degradation than most other gasoline components. As a result, historically contaminated soil may not contain measurable quantities of benzene and certain other BTEX compounds. Leachate testing of soils can be used, in conjunction with total BTEX concentrations, for determining the allowable soil concentrations for the soil leaching to groundwater migration pathway.

4.2 Trimethylbenzene (TMB)

The TMB isomers (1,2,3-TMB, 1,2,4-TMB and 1,3,5-TMB), and iso- and n-propylbenzenes are constituents of leaded, unleaded and aviation gasolines, kerosene, JP-4, diesel fuel and #2 fuel oil. These compounds are often present in petroleum products at greater concentrations than the BTEX compounds. The analytical methods listed in the STD Operational Memorandum #14 are not capable of detecting 1,2,3-TMB. The DEQ has not established Tier I risk-based screening levels (RBSLs) for 1,2,3-TMB and n-propylbenzene. Therefore, this section will focus on 1,2,4-TMB, 1,3,5-TMB and isopropylbenzene.

The TMB isomers generally fall between xylenes and naphthalene in terms of their volatility and mobility in the soil and groundwater. The TMB isomers and isopropylbenzene are unlikely to be of concern for the inhalation and direct contact exposure pathways. The TMB isomers may have the most restrictive RBSLs for the soil leaching to groundwater and groundwater drinking water ingestion pathways when benzene is not present above its RBSLs. Isopropylbenzene, because its RBSLs are not more restrictive than the other BTEX compounds, is unlikely to have the most restrictive RBSLs at a LUST release facility.

The TMB isomers and isopropylbenzene are generally considered to be less amenable to biodegradation than the BTEX compounds. They may be present in the soil and/or groundwater above their respective RBSLs after the BTEX compounds have biodegraded. Because of their lower volatility, they may still be present above their RBSLs after the BTEX compounds have been remediated by an air-based remediation system (e.g., SVE and air sparging).

4.3 Methyl tert-Butyl Ether (MTBE)

MTBE is added to gasoline at concentrations from 2-7% and is restricted to 15% by volume. MTBE is blended into regular, unleaded, and unleaded premium grades to increase octane ratings. The highest levels are found in the higher octane unleaded gasolines (premium unleaded). At 4.3% solubility in water, it is among the most water soluble compounds present in gasoline. Since adsorption to soils is inversely proportional to solubility, MTBE is one of the first gasoline constituents to leach out of soil. It also separates in groundwater, and moves ahead of other gasoline components in groundwater. MTBE is therefore a potentially valuable monitoring parameter, and precursor of gasoline contamination since it may form a "halo" along the leading edge of the plume.

The presence and concentration of MTBE may also be important for design of cleanup remedies. For these reasons, MTBE is a required parameter for investigation and cleanup of unleaded gasoline contaminated groundwater and soil. The value of MTBE as a monitoring parameter is significantly reduced by analytical detection limits of 50 μ/l in water and 100 μ/kg soil. Leachate testing of soil, accompanied by total MTBE concentrations, is an acceptable option for establishing site-specific concentrations that are protective of the soil leaching to groundwater pathway.

4.4 Ethylene Dibromide (EDB)

EDB (a.k.a. 1,2-dibromoethane) is a leaded gasoline additive and former pesticide. In the 1970s and early 1980s, it was used as a soil fumigant to protect fruits, vegetables and grain crops from insect pests and nematodes. It was also used as a soil fumigant on turf grass, and particularly on golf courses. In 1984, the use of EDB as a soil and grain fumigant was banned. Since the use of leaded gasoline has been greatly reduced, less EDB is made for addition to leaded gasoline.

EDB is very mobile in the soil and groundwater and can be found at the leading edge of a contaminant plume. It is very toxic and has extremely low RBSLs (see the STD Operational Memorandum #4, Tier 1 Lookup Tables for Risk-Based Corrective Action at Leaking Underground Storage Tank Sites). If detected, EDB is likely to be above the soil and groundwater direct contact RBSLs. For these reasons, EDB has been added to the list of recommended parameters for leaded gasoline, and leaded aviation gasoline releases.

4.5 1,2-Dichloroethane (1,2-DCA)

1,2-DCA is currently used as a chemical intermediate, such as in the synthesis of vinyl chloride, vinylidine chloride, and other compounds, and as a scavenger compound for addition to leaded gasoline. Former uses include use in varnish and finish removers; in soaps and scouring compounds; in dry cleaning solvents; in metal degreasers; in paints, coatings, and adhesives; as a grain fumigant; household fumigant; and soil fumigant. 1,2-DCA in soil may leach to groundwater since the compound does not adsorb to soil particles unless the organic content of the soil is high. 1,2-DCA is expected to undergo little or no biological degradation in aquatic systems. The lifetime of 1,2-DCA in groundwater is on the order of days to years. 1,2-DCA in soil is expected to volatilize or leach to groundwater before undergoing significant abiotic transformation. The rate of biodegradation in soils is unknown. 1,2-DCA is very mobile in the groundwater and may be found at the leading edge of a contaminant plume.

4.6 Polynuclear Aromatic Hydrocarbons (PNAs/PAHs)

PNAs are a group of chemicals composed of from two to five fused benzene rings that are formed during the incomplete combustion of coal, gas, wood, and other organic substances. PNAs can be man-made or naturally occurring. They are ubiquitous products of combustion from common sources such as motor vehicle exhaust and exhaust from other internal combustion engines, wood burning stoves, cigarette smoke, and industrial smoke or soot. There are more than 100 different PNA compounds. They can be found in substances such as crude oil, coal, coal tar pitch, and road and roofing tar. PNAs are ubiquitous in soil. Concentration of individual PNAs are usually less than 100 ppb in rural soils, generally less than 200 ppb in agricultural soil, and may be in the range of 100 ppb to 100 ppm in urban soils. Cleanup based on site specific background levels may be appropriate on rural, agricultural, and urban sites. PNAs are present at 1-2% by weight in crude oils. Certain compounds may also be found in refined petroleum products including gasoline, kerosene, diesel oil, some heating oils, and motor oil. Leachate testing of soil, accompanied by total PNA concentrations, is an acceptable option for establishing acceptable concentrations in soil for the soil leaching to groundwater migration pathway.

4.7 Cadmium

Analysis of cadmium is required in the evaluation of used motor oils and waste oils. Cadmium must be measured as dissolved cadmium in groundwater. Samples for measurement of dissolved metals may be filtered at the analytical laboratory, provided that the sample is filtered and then preserved within 24 hours of the sample collection. Since changes in the water sample’s pressure, pH and/or dissolved oxygen concentration can alter the sample chemistry (e.g., by causing dissolved metals to precipitate), the most representative groundwater samples are field-filtered immediately after collection, preserved, and transported to the laboratory. Dissolved metal samples should not be preserved prior to filtration since the preservative may remobilize metals that were adsorbed onto sediment in the sample. The recommended method of sample filtration is to use an in-line cartridge filter. In soils, cadmium may be measured as either total cadmium or leachable cadmium using a soil leachate procedure identified in Table 3 of this document. Total metal samples should be collected along with leachable metal samples to allow for a direct comparison between the total and leachable concentrations.

4.8 Chromium

Analysis of chromium is required in the evaluation of used motor oils and waste oils. Chromium may be measured as total chromium, or as hexavalent and trivalent chromium. If only total chromium is measured, then hexavalent chromium cleanup values must be used. Total chromium cleanup values (target method detection levels or default background values) may be used if hexavalent chromium levels are below target method detection limits based on measurement of representative soils. If trivalent and hexavalent chromium are measured, their respective cleanup limits apply. Trivalent chromium may be determined by subtraction of hexavalent chromium from total chromium. Target method detection limits for trivalent chromium are the same as those listed for total chromium.

Chromium must be measured as dissolved chromium in groundwater. Since changes in the water sample’s pressure, pH and/or dissolved oxygen concentration can alter the sample chemistry (e.g., by causing dissolved metals to precipitate), the most representative groundwater samples are field-filtered immediately after collection, preserved, and transported to the laboratory. Dissolved metal samples should not be preserved prior to filtration since the preservative may remobilize metals that were adsorbed onto sediment in the sample. The recommended method of sample filtration is to use an in-line cartridge filter. In soils, chromium may be measured as either total cadmium or leachable cadmium using a soil leachate procedure identified in Table 3 of this document. Total metal samples should be collected along with leachable metal [illegible] he total and leachable concentrations.

4.9 Lead

Lead is a required monitoring parameter for releases involving leaded gasoline (or unknown gasoline), used motor oil, and waste oils. The lead in gasoline is present as organolead compounds at concentrations ranging between 13 and 1100 mg/l as lead. Lead is also present in used motor oil and in some waste oils. Lead must be measured as dissolved lead in groundwater. Since changes in the water sample's pressure, pH and/or dissolved oxygen concentration can alter the sample chemistry (e.g., by causing dissolved metals to precipitate), the most representative groundwater samples are field-filtered immediately after collection, preserved, and transported to the laboratory. Dissolved metal samples should not be preserved prior to filtration since the preservative may remobilize metals that were adsorbed onto sediment in the sample. The recommended method of sample filtration is to use an in-line cartridge filter. In soils, lead may be measured as either total cadmium or leachable cadmium using a soil leachate procedure identified in Table 3 of this document. Total metal samples should be collected along with leachable metal samples to allow for a direct comparison between the total and leachable concentrations.

4.10 Volatile Halocarbons

Volatile halocarbons (a.k.a. solvent compounds) are necessary for the investigation and cleanup of used oil and waste oil releases since volatile halocarbon solvents are contained in many products used to clean or service automobile parts. These solvents may also be mixed into waste oils from a variety of sources. Other volatile organic compounds should also be evaluated whenever there is reason to believe that other non-petroleum volatile organic compounds might be present.

4.11 Polychlorinated Biphenyls (PCBs)

PCBs are necessary for the investigation of waste oil releases since transformer and capacitor fluids containing PCBs, and PCBs from other sources, have been commonly associated with waste oils. PCB analysis may be performed as individual aroclors (1016, 1221, 1232, 1242, 1248, 1254, and 1260), or as total PCBs. In those cases where more than one aroclor is determined, the sum of the individual aroclors should be compared to the applicable cleanup levels for total PCBs.

5.0 MONITORING PARAMETERS FOR CLEANUP OF COMMON PETROLEUM PRODUCTS

Table 1 provides guidance for selection of appropriate parameters for investigation, monitoring, and closure of various petroleum hydrocarbon product releases. Other compounds may need to be considered depending on the nature and severity of the release, or on permit requirements for liquid or solid wastes. The appropriate waste disposal facility and/or permitting division in the Department of Environmental Quality should be contacted, as appropriate, to determine other necessary parameters or applicable limits.

5.1 Gasoline

Investigation and cleanup verification of gasoline releases is based primarily on benzene, toluene, ethylbenzene, and xylene (BTEX). BTEX is particularly well suited for evaluating gasoline releases to groundwater since these compounds are among the most soluble gasoline constituents. In addition to BTEX, other required monitoring and cleanup verification parameters for gasoline include: lead, 1,2,-dichloroethane (1,2 DCA), and ethylene dibromide (EDB) for leaded gasoline, MTBE for unleaded regular and premium grades, and naphthalene, 2-methylnaphthalene, 1,2,4-trimethylbenzene (TMB), and 1,3,5-TMB for investigation and cleanup verification in all gasoline releases. The value of measuring these last four compounds is due to their characteristics which allow them to remain in soil after other indicator parameters have degraded, leached away, or volatilized. Other PNA compounds present in low mg/kg levels include acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, and fluoranthene. These compounds have been found in soils associated with gasoline releases but closure is nearly always based on other compounds.

5.2 Petroleum Solvents

Petroleum solvents do not usually contain sufficient quantities of target analytes (BTEX and PNAs) to allow their measurement in soil and water samples. If, after initial analysis, the target analytes are not detected, the measurement of petroleum solvents may be based on the GRO procedure, which quantifies all chromatographic peaks between 2-methyl pentane and 1,2,4-trimethylbenzene. Site closure may be based on achieving target MDL criteria. Target MDL criteria for groundwater and soils using the GRO method are 200 ug/l and 5000 ug/kg, respectively. Please refer to Section 6.2.5 for additional guidance on the GRO method.

5.3 Light Distillate Fuel and Diesel Oils

Parameters for investigation and cleanup verification of light distillate fuel and diesel oil releases (kerosene, fuel oils 1 and 2, diesel oils 1-D and 2-D, and jet fuels JP-4, JP-7, JP-8, and Jet A) include BTEX, PNA, and TMB compounds. BTEX compounds (with the exception of JP-4) are not particularly good monitoring parameters for these light distillate oils since they are present in only trace amounts or absent. PNAs are better monitoring compounds since they range from low levels to approximately 5%. If target analytes are not present and further cleanup is necessary to eliminate aesthetic impacts in groundwater or soil, the DRO target MDLs may be used in conjunction with a risk based corrective action (RBCA) evaluation to achieve closure. Target MDLs for groundwater and soils using the DRO method are 100 µg/l and 4000 µg/kg, respectively. Please refer to Section 6.2.5 for additional guidance on the DRO method.

5.4 Residual Oils, Lubricating Oils, and Hydraulic Oils

Measurement of PNAs and TMBs is required for investigation and cleanup verification in residual fuel oils (fuel oils 4, 5, and 6 and diesel oil 4-D). BTEX compounds may be absent or present in only trace quantities in this group of oils and are, therefore, not a required parameter. PNA compounds in this group of oils are present at low levels (lubricating oils) to higher levels (>5%) in residual heating oils.

Previous experience with the use of PNAs in final investigation and cleanup verification has shown that PNAs are occasionally undetectable in cases where soils are stained and have objectionable odors (apparently due to the abundant alkanes and cycloalkanes in these oils). If target analytes are not present and further cleanup is necessary to eliminate aesthetic impacts in groundwater or soil, the DRO target MDLs may be used in conjunction with a risk based corrective action (RBCA) evaluation to achieve closure. Target MDLs for groundwater and soils using the DRO method are 100 µg/l and 4000 µg/kg, respectively.

5.5 Waste Oil and Used Motor Oil

Required parameters for measurement of used motor oil include BTEX, cadmium, chromium, lead, EDB, 1,2-DCA, PNAs, TMBs and volatile halocarbons. Parameters for waste oil include these same parameters, plus PCBs.

Since nearly any type of waste could conceivably be mixed with “waste oil”, this parameter list is by no means fixed. Other parameters can and should be added consistent with information about the source of the waste. Other metals, cyanide, sulfide, chlorinated hydrocarbons (extractable), and other compounds may be present.

PNAs are formed in the combustion chambers of internal combustion engines and concentrated in the motor oil. Levels of various individual PNAs found in used motor oil are commonly in the 10-20 mg/kg range and have been measured up to 500 mg/kg. These levels in used oil contrast levels in new lubricating oil which are often near the range of detectability up to about 0.3 mg/kg. If target analytes are not present and further cleanup is necessary to eliminate aesthetic impacts in groundwater or soil, the DRO target MDLs may be used in conjunction with a risk based corrective action (RBCA) evaluation to achieve closure. Target MDL for groundwater and soils using the DRO method are 100 µg/l and 4000 µg/kg, respectively.

5.6 Unknown Petroleum Products

In the case of developing a monitoring strategy for unknown petroleum products, a phased sampling/analytical approach is often valuable. Initial high concentration samples are analyzed using potential analytical methods to identify the most appropriate method(s). After the most appropriate analytical method(s) have been identified, site characterization and cleanup can proceed using the appropriate methods.

Initial analytical parameters should include BTEX, TMBs, EDB, 1,2-DCA, PNA compounds, volatile halocarbons, cadmium, chromium, and lead. If these compounds are not detected, <u>and</u> there are no aesthetic groundwater impacts, <u>and</u> there are no aesthetic soil impacts, site closure may be appropriate.

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For sites where the above compounds are not detected, and aesthetic impacts to soil or groundwater are present, both GRO and DRO methods should be performed. These non-specific test procedures are useful for those petroleum products which may not contain measurable quantities of BTEX or PNA compounds. Target MDL criteria or aesthetic criteria are acceptable for demonstrating cleanup. Please refer to Section 6.2.5 for additional information regarding the DRO and GRO procedures.

In lieu of conducting the non-specific DRO or GRO methods, a volatile and/or semivolatile library search may be performed as indicated by the physical characteristics (volatile, non-volatile, light, heavy, etc.) of the petroleum product. Please refer to Section 6.2.6 for additional information regarding library searches.

5.7 Other Products

In the case of other petroleum products or additives where the product name or chemical name is known, the parameters should be selected based on the information about the product such as might be contained in product labeling or Material Safety Data Sheets. Material Safety Data Sheets often provide useful information for selecting the appropriate method.

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6.0 METHODS FOR MEASUREMENT OF PETROLEUM PRODUCTS AND CONSTITUENTS

Petroleum and petroleum products are diverse, and field and lab methods required for analysis of petroleum and petroleum products are also diverse. Few analytical methods by themselves have the ability to provide all the information necessary for cleanup and investigation of petroleum products. Methods are designed to evaluate certain fractions, certain compound groups, or as total product analyses. The quality and sophistication of the analysis varies considerably from inexpensive field screening procedures to very sophisticated laboratory analyses. The suitability of these various procedures depends on the questions to be answered by the data. The following section describes analytical methods commonly used to investigate petroleum losses. (Reference to products is intended for purposes of illustration, and is not meant as an endorsement of the product by the State of Michigan.)

6.1 Field Measurements

Field measurement procedures reduce the time required to conduct a site assessment. Field measurement procedures provide rapid, qualitative, semi-quantitative, or quantitative, on-site information about the severity and extent of contamination. This information can be effectively used to direct additional investigations, determine monitoring well locations, and make other cleanup decisions. Field measurements reduce the loss of contaminants in the sample container due to volatilization and biodegradation. Moreover, the lower cost of field measurements can reduce the cost of the investigation, allowing more samples to be collected at the site, giving a clearer picture of the extent of the release, and providing better cleanup decisions.

Equipment for field analysis and screening of organic compounds falls into four broad categories:

- Soil Screening by Immunoassay
- Portable, Total Organics Vapor Monitors
- Portable, Selective Organic Instruments
- Mobile, Selective Organic Instruments

6.1.1 Screening by Immunoassay

The sensitivity of the Enzyme immunoassay test depends on the binding of the target analyte to the antibodies used in the kit. The antibody may be specific to one compound or a family of compounds, e.g., total BTEX or total PNAs. In those tests which respond to a group of compounds e.g., BTEX compounds, the response to these various compounds may be different for each chemical and may include other non-target chemicals. Consequently, there are no comparable laboratory analytical procedures to judge the performance of such tests.

Immunoassay test kits are offered for a variety of pesticides, PCBs, “total BTEX” and “total PNAs” by several different manufacturers. Method 4030, Soil Screening for Petroleum Hydrocarbons by Immunoassay, has been added to SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA Office of Solid Waste). The method can be used to locate areas of low range (40-100 ppm), medium range (100-1000 ppm), and high range (>1000 ppm) hydrocarbon levels. The kit used in Method 4030 is most sensitive to the small aromatic hydrocarbons (e.g., ethylbenzene, xylene, and naphthalene) found in fuels and is relatively insensitive to large compounds found in oils and greases. The technique may be useful for delineating gasoline contaminated soil at 40 ppm and above. Other manufacturers of "total BTEX" test kits claim sensitivities as "low as 5 ppb for benzene levels" for water samples and low part per million levels in soil. Immunoassay test kits for measurement of total PNA hydrocarbons claim detection capabilities of 50 ppb in water and 1 ppm in soil. PCB immunoassay test kits are capable of detecting low ppb levels in water samples and approximately 50 ppm in soils. Performance of immunoassay procedures is often stated in terms of percent agreement with a gas chromatograph (GC) or gas chromatograph/mass spectroscopy (GC/MS) procedure. For example, if an immunoassay test for PCBs stated 90% agreement with Method 8082, it means that when PCBs are above a certain level (as determined by Method 8082) the immunoassay procedure will agree that PCBs are over a certain level 90% of the time.

6.1.2 Portable, Total Organic Vapor Monitoring

Equipment in this category includes the HNU Model 101, the AID Models 710/712 and 580, and the Foxboro OVA 108/128. These instruments are essentially battery operated gas chromatographic detectors, without chromatographic columns, that continuously sample ambient air. They respond to all organic vapors and are non-selective. The HNU Model 101, and the AID Model 580, both use a Photoionization Detector (PID). The PID does not respond to methane (or any other organic molecule with an ionization potential greater than the energy of the ionizing lamp). This selective response is an advantage since methane is a common organic decomposition product and does not necessarily indicate the presence of petroleum products. PIDs equipped with 9.5 eV, 10.2 eV and 11.7 eV lamps all have high responses to benzene, ethylbenzene, toluene, and xylenes. These meters accept only vapor state samples which limits the type of sample and also restricts the range of measurable compounds or products to the relatively volatile materials.

Relying solely on field screening results for important site management decisions is not recommended. Several factors contribute to the differences between laboratory and field data. The most prominent factors are the characteristics of the particular hydrocarbon and especially volatility. Visual observation coupled with the use of field instrumentation may be the most cost-effective technique for field screening soil samples, but such procedures should only be used as general indicators of soil contamination. Some soil samples that appear clean in the field should be tested using validated analytical procedures as a check on samples selected based on field screening techniques.

6.1.3 Portable Selective Organic Instruments

This group of instruments includes the Photovac 10A10, the AID Model 511, and the Foxboro OVA Century. While these instruments are portable, they are not as simple to use as the total organic vapor instruments. All are isothermal gas chromatographs. The Foxboro is designed to operate at either 0 or 40 ^{0}C while the Photovac operates at ambient temperature. Neither instrument is appropriate for the analysis of naphthalene and larger compounds. The AID GC will maintain a 200 ^{0}C column oven temperature on battery power for 8 hours, if the oven is first preheated on AC power. This elevated temperature capability makes the AID suitable for field analysis of naphthalene, and other somewhat larger semivolatile compounds and also allows injection of liquid samples. These instruments are capable of identifying and quantifying organic compounds in relatively non-complex samples, but the presence of large numbers of compounds seve[illegible]quantify target analytes.

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6.1.4 Mobile, Selective Organic Instruments

This group of instruments is dependent on AC power for operation but is mobile in the sense that they can be operated in a trailer or vehicle equipped with an AC generator or with access to a suitable power drop. Certain instruments incorporate special design considerations which allow them to be more easily set up, transported, and adapted to mobile situations. Realistically, almost any instrument that can be operated in a fixed laboratory can also be operated in a trailer or motor home. The advantage of mobile instruments is that they offer most of the selectivity and sensitivity of lab instruments and many of the advantages of portable instruments. Transportation and set up costs are significant and, consequently, there must be an adequate sample load to keep the costs competitive with fixed laboratory analyses. Effective use of these instruments requires a high level of expertise and experience. Purge and trap GC instruments are commonly operated in mobile situations for investigation of gasoline releases.

6.1.5 Vapor Measurement Techniques

The vapor measuring instruments discussed in the preceding paragraphs are used to make direct measurements of site vapor, to measure vapor in the headspace over the sample, and to make direct measurements of soil vapor. These vapor measurements yield reasonably representative estimates of water and soil contaminant concentrations when the petroleum product contains volatile constituents. Vapor measurements should not be used in those cases where the petroleum contamination is primarily or completely composed of non-volatile constituents. The headspace method and soil vapor methods are described below. Alternatively, vapor samples can be collected and transported to a fixed laboratory.

6.1.5.1 Headspace Analysis of Soil and Water Samples

This procedure involves collecting a soil or water sample in an air tight container, and then analyzing the headspace vapor using a portable analytical instrument. Samples are frequently agitated (water) or heated (water and soil) to better volatilize light hydrocarbons. Headspace techniques are very simple and can be conducted quickly with minimal equipment and operator experience. Results are qualitative and are used to help define the boundaries of soil contamination and to determine where to set well screens as wells are constructed.

6.1.5.2 Soil Vapor Sampling and Analysis

This procedure involves measuring the volatile hydrocarbon concentrations in a soil vapor sample collected by pumping the vapor out of the soil vadose zone, collecting a vapor sample, and analyzing the sample. The most common procedure for collecting the vapor sample involves driving a hollow steel probe into the ground, extracting the soil vapor under vacuum, and collecting the vapor with a syringe for injection into a field gas chromatograph equipped with flame ionization or photoionization detectors. The skill level required to perform the procedure depends greatly on the analytical instrument. Soil vapor measurements are used to provide an indirect estimate of the vertical and lateral extent of soil and shallow groundwater contamination, to identify areas of potentially high contamination, and to determine locations for installation of groundwater monitoring wells. However, the procedure cannot be used to determine the concentration of [illegible] valuating the level of contamination relative to other [illegible]

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6.1.6 Field Measurement Guidelines

The use of portable field instrumentation for either total or selective organic constituents to guide remedial activities and response actions is encouraged. The use of field instrumentation may also be used to guide sample selection for sampling done to demonstrate compliance with cleanup levels. Field screening is appropriate for investigations where the objective is to collect preliminary information about a release with lab confirmation of the preliminary information. An important requirement of any field screening technique is that the field screening technique be sensitive enough to measure levels of concern so that significant contamination is not over looked during preliminary portions of the investigation. Where sensitivity is inadequate, suitable laboratory or mobile lab measurements must be used to verify the field screening measurements. Specifically, field vapor measurements are appropriate in the following situations:

- To measure appropriate contaminants. Vapor measurement techniques are appropriate for volatile compounds; vapor measurements are not appropriate for semivolatile, non-volatile contaminants, or metals.

- To identify and delineate horizontal and vertical soil and shallow groundwater contaminant boundaries with adequate lab confirmation.

- To make preliminary identifications of contaminants and contaminant levels with adequate laboratory confirmation.

- To identify future sampling locations, to locate monitoring wells, and to vertically locate well screens.

- To bias sampling locations toward likely remaining areas of contamination in cleanup verification sampling.

It is difficult to provide rigid or numerical guidelines concerning the number of lab measurements necessary to confirm field screening data. The most important consideration in the use of screening data is the relationship between field screening measurements and lab measurements, assuming that such a relationship exists. In those cases where the relationship is unknown, or poorly known, the number of field measurements to be confirmed by lab measurements should be sufficient to demonstrate this relationship. The particular use to be made of the field screening data in making site management decisions is an important consideration concerning how well this relationship must be defined. Data used to make preliminary site decisions may not need immediate or concurrent confirmation; however, data used to verify final cleanup must be confirmed.

There should be a reasonable correlation between vapor measurements in the field and purge and trap laboratory measurements assuming the same detector is used for the same target analytes. For example, very old gasoline will have enough non-BTEX compounds present to give a positive reading on vapor measuring instruments, but laboratory targeted BTEX compounds may not be detected. The temperature at which the vapor measurement is made in the field has a direct affect on what is measurable. Verification of final cleanup must be based on lab data or mobile lab data supported by proper QA/QC.

6.2 Laboratory Methods

6.2.1 Acceptable Methods and Target Method Detection Levels (TMDLs)

Any of the analytical methods listed in Table 2 of this guidance are appropriate for the parameters identified in this document. This listing of analytical methods includes multiple methods in those cases where more than one method is appropriate to allow flexibility in the selection and use of analytical methods. These methods were selected based on the need to measure contaminants at or below the lowest of the applicable cleanup levels. If there are no analytical methods capable of measuring the appropriate levels, the target MDL is established as low as practical and methods are listed accordingly. The target method detection limits, as listed in Operational Memorandum #4 Look up Tables for Risk Based Corrective Action at Leaking Underground Storage Tank Sites (Op-Memo #4), are necessary for measurement of the most restrictive cleanup criteria; however, other method detection limits may be acceptable for other criteria.

In the case of metals, the background levels or the default background criteria listed in Op-Memo #4, may be well above risk based or detection based levels. Less sensitive methods (higher detection limits) may also be acceptable for other data usage purposes, such as in the case of preliminary site evaluation work or to determine off-site waste disposal requirements. Less sensitive methods are also acceptable when the sample concentration (prior knowledge of sample levels is necessary) is within the analytical range of the selected less sensitive method, regardless of the particular target cleanup concentration. For example, Method 6010V, Inductively Coupled Plasma (ICP) is acceptable for measuring naturally occurring elements (metals) in soil and groundwater when the sample concentration is within the working range of the ICP method, even though ICP may not achieve TMDLs found Op-Memo #4. If the sample concentration is below the ICP range, then a more sensitive technique may be necessary to allow evaluation of a lower cleanup level. Ideally, the method detection level should be at least one-third to one-fifth of the cleanup level being evaluated.

6.2.2 Sample Introduction and Extraction Techniques

The first step in the analysis of organic compounds contained in petroleum hydrocarbons in soil and groundwater samples is to separate the constituents from the soil or water matrix. This is commonly done by purge and trap or by solvent extraction procedures.

6.2.2.1 Purge and Trap (P & T)

Purge and trap techniques bubble an inert gas through the sample in a specially designed purging chamber and transfer the volatile constituents from the sample into a trap where the constituents are absorbed and concentrated on charcoal and other absorbent materials. Purging may be performed at ambient temperature, or at an elevated temperature to improve purging efficiencies for less volatile or more water soluble compounds.

When the purge and trap step is complete, the trap is heated and back flushed to the column in a stream of inert gas. Volatile compounds are separated in the column and are quantified by various detectors as they elute from the column. The purge and trap technique is appropriate for compounds that are slightly soluble in water and boil at less than approximately 200 °C. The technique is extended to other compounds that are more water soluble or have higher boiling points by performing the purge at an elevated temperature. The sensitivity of purge and trap techniques can be improved by using a larger purging chamber, and increasing the sample size or by using a more sensitive detector or both.

6.2.2.2 Solvent Extraction (SE)

Solvent extraction is used to separate the larger semivolatile compounds, with boiling points beyond the range of volatile compounds. Various organic solvents or solvent combinations are used. The efficiency of the extraction for particular compounds is determined by choice of solvent. When large numbers of compounds are extracted, as is the case with petroleum hydrocarbons, the solvent is selected based on its overall ability to dissolve the target analytes. The solvent may not efficiently dissolve some compounds. In the case of petroleum hydrocarbons, many of the very large and higher boiling point hydrocarbons present in asphaltenes and tars may not dissolve in common organic solvents such as hexane, methylene chloride, and freon. Fortunately, these compounds are essentially insoluble in water and are relatively immobile in soil, and therefore present less of a threat to groundwater.

Water samples are extracted by liquid: liquid extraction techniques which shake or agitate a mixture of water and solvent. Target analytes with greater affinity for the solvent move from the water phase to the solvent phase; the solvent is then separated from the water sample, concentrated, and injected into the heated inlet of chromatographic column where it is vaporized and swept through the column by the carrier gas. Analytes eluting from the column are determined by a detector suitable for the target analytes.

Sonication, and Soxhlet are two common extraction procedures used to extract petroleum hydrocarbons from soil samples. In sonication (or ultrasonic extraction) the soil sample is dried with sodium sulfate, solvent is added and the soil/solvent mixture is then subjected to ultra-sonic vibrations which provide intimate contact with the solvent and the soil particles. The duration of the sonication step is three minutes with unheated solvent. The method is not appropriate for extracting thick hydrocarbons from dense soils.

With Soxhlet extraction the soil is again dried with sodium sulfate and solvent, and the soil sample is placed in the Soxhlet apparatus where condensed solvent repeatedly passes through the soil held between two glass wool plugs. The Soxhlet method requires 8-16 hours of vigorous heated reflux, and is appropriate for semivolatile hydrocarbons in all types of soils. As with water samples, the solvent volume is reduced by evaporation, thereby concentrating the extracted compounds, and the extract is analyzed.

6.2.3 Analysis

After purge and trap or extraction, the second step is to quantify the constituents. The two basic approaches to analysis of petroleum and its products may be categorized as specific methods and non-specific methods. Specific methods are directed at the individual compounds. Non-specific methods are directed at some fraction of the range of petroleum compounds as defined by the conditions of the method.

6.2.4 Specific Methods

If information is needed about the identities of individual constituents, the constituents in the extract are separated by chromatography and the eluted compounds are identified and quantified using a variety of methods and detectors. Volatile petroleum constituents, separated from water and soil samples by purge and trap techniques, are chromatographed and quantified by Hall Electrolytic Conductivity Detector (HECD), Photoionization Detector (PID), Flame Ionization Detector (FID), or Mass Spectrometer (MS). The HECD is selective for volatile halocarbons; the PID is highly responsive to volatile aromatic compounds and other compounds with ionization potentials within the range of the detector. The FID is a good general detector for petroleum hydrocarbons, and the MS is appropriate for petroleum hydrocarbons and other compounds within the mass range of the instrument.

Semivolatile constituents are separated from the matrix by solvent extraction, these constituents are separated by chromatography, and quantified by FID, MS, or Ultra-Violet (UV), and Fluorescence (Fluor). Separation of individual constituents is limited by the chromatographic column and these limitations become more severe as the number of compounds to be separated increases, and with increasing molecular weight and boiling point of the individual constituents. Separation of volatile constituents is within the capabilities of modern capillary columns. However, in the semivolatile fraction, separation of individual constituents becomes geometrically more difficult as the number of carbons in the molecule and the number of isomers increases. For example, C_5 isoalkane has two possible structural isomers, and C_9 has 34 possible isomers. It is extremely difficult to separate C_9 and higher isomers.

6.2.4.1 Volatile Organic Compounds

Volatile Organic Compounds are measured via GC/PID Methods (e.g., Method 8021) or GC/MS (e.g., Method 8260). The GC/MS methods are capable of measuring both aromatic and halocarbons simultaneously. GC methods which use PID and HECD detectors in series are also capable of measuring aromatics and halocarbons simultaneously.

6.2.4.2 Polynuclear Aromatic Hydrocarbons (PNAs)

GC/MS (e.g., Method 8270) and High Pressure Liquid Chromatography (HPLC) (e.g., Method 8310) methods are recommended for analysis of PNAs. Naphthalene and 2 methylnaphthalene are required to assess old gasoline releases and in-situ remediation of old gasoline sites. Either PNA or volatile methods may be used for analysis of naphthalene and 2 methylnaphthalene.

6.2.5 Non-specific Methods

Non-specific methods are designed to provide a total value which represents either the product (gasoline, fuel oil, etc.) or all hydrocarbon compounds measurable under the conditions of the particular analysis. Non-specific methods are of little value in the determination of risk based values since results from non-specific methods do not identify specific constituents and risk based values are usually based on specific constituents. However, non-specific methods are useful for some products where PNAs, TMBs or BTEX compounds are not present in sufficient quantities in the product to allow them to be measured. Examples of such uses include the use of the GRO method for evaluating petroleum solvent releases and the DRO method for evaluating aesthetic impacts. Because of the variability of petroleum products in terms of volatility, boiling point, molecular weight, carbon number, solubility, and etc., no single non-specific method is suitable for analysis of each and every petroleum hydrocarbon product.

The following table compares the separation, range of analytes, boiling point, and detection levels of common GRO and DRO methods used to evaluate petroleum hydrocarbons. The individual components are separated by chromatography, and detected (but not identified) separately. Results are reported as a total product.

Method	Prep./ Ext.	Analytes/ Carbon #	Boil. Pt. Range (°C)	Target MDL Water	Target MDL Soil
GRO	P & T	Vol. C6-C10	60 - 170	200 ug/l	5000 ug/kg
DRO	SE	Ext. C10-C28	170 - 430	100 ug/l	4000 ug/kg

The GRO and DRO Methods are designed to evaluate various types of petroleum releases, and provide useful information about the kinds of petroleum compounds and products remaining in the environment.

The following non-specific methods are identified for use in evaluating petroleum solvents or aesthetic groundwater impacts arising from contaminated soil (where BTEX and PNAs are absent) and stained soils or soils producing objectionable odors. Target MDL criteria or aesthetic criteria are acceptable for demonstrating cleanup. These methods are listed below.

6.2.5.1 Gasoline Range Organics (GRO)

Samples are analyzed using purge and trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by flame ionization detector (FID) or FID with Photoionization detector (PID) in series. Quantification is based on FID detector response to a gasoline component standard. The optional addition of a PID detector in series (or substituting a MS detector for the FID and PID) allows simultaneous measurement of BTEX compounds. Simultaneous measurement of BTEX compounds is acceptable provided that suitable detection levels can be achieved. The method is suitable for analysis of waters, soils, or wastes. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents and the methanol is analyzed by purge and trap GC as a water sample. GRO is defined as all chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene.

Quantification is based on a direct comparison of the area within this range to the total area of the 10 component standards. This range includes the majority of the most abundant gasoline constituents including the methyl-, dimethyl-, trimethyl- pentanes, hexane, methyl-, dimethyl-, trimethyl- hexanes, heptane, benzene, toluene, ethylbenzene, xylenes, and certain alkalated benzenes. The alkanes are less water soluble than aromatic compounds and are likely to remain in soils after the aromatic compounds have leached away or degraded.

6.2.5.2 Diesel Range Organics (DRO)

Similarly, the Diesel Range Organic Method uses an FID detector. Calibration and quantitation is based on 10 alkanes. DRO results provide better information about the range of contaminants in products such as fuel oil, diesel oil, lubricating [illegible] on a few target compounds which are not particularly [illegible]

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The method is designed to measure mid-range petroleum products such as diesel or fuel oil. One liter of water or 25 grams of soil is extracted (sonication) with methylene chloride. The extract is dried, concentrated, and injected into a capillary column GC equipped with FID detector. Quantitation is performed by comparing the total chromatographic area between decane (C_{10}) and octacosane (C_{28}), including resolved and unresolved components, to the response of a 10 component calibration standard. Components greater than C_{28} present in products such as motor oils, lubricating oils, or crude oils will show up in the chromatogram under the conditions of the analysis, but will not be quantified or reported unless specific arrangements are made with the laboratory. The lab should extend the method to include the dominant components of the product. If the presence of such products is indicated, they may be quantified through additional efforts such as analysis of additional standards. These additional steps are not described in the method. An MS detector may be substituted for the FID detector to provide simultaneous measurement of DRO and PNA compounds.

6.2.6 GC/MS Library Searches

GC/MS Library Searches are one alternative for measuring or identifying unknown products.

The USEPA Contract Laboratory Program identifies procedures for performing volatile and semivolatile library searches for both soil and water samples. Procedures for the 10 peak volatile library search and the 20 peak Base/Neutral/Acid extractable library search are identified in the USEPA Contract Laboratory Program, Statement of Work, for Multi-Media, Multi-Concentration Organic Analysis. The library search provides tentative determination of the top 10 or 20 most abundant non-target compounds. Compounds reported from a library search are reported as tentatively identified compounds (TICs) with the probability of a correct match to the library spectra. The need to confirm TICs data is based on the importance of the compound in comparison to other compounds or elements known to be present at the site and indirectly on such factors as the concentration, toxicity, risk, routes of exposure, reliability of the identification, presence of other contaminants which might control the extent of cleanup, and the ability of the site remedy or remedies to remove the tentatively identified compounds.

Identification of the major constituents in a petroleum product will facilitate achieving appropriate cleanup criteria. Adequate toxicity data for each constituent is a prerequisite for establishing risk based cleanup and may limit the use of this approach.

If the library search provides TICs, the tentative identifications should be confirmed, if necessary and possible. Cleanup to established limits can be performed if such limits are available for the identified compounds. If no limits are available from the DEQ and suitable information does not exist for development of such limits, the alternatives are to develop LD_{50} data, to use data from similar compounds as a surrogate or indicator, or to cleanup to aesthetic impact limits.

If there are no tentative identifications, or aesthetic impacts, then site closure may be appropriate. If the library search identifies non-specific contaminants (e.g., unknown alkanes, alkalated aromatics, or unknown cycloalkanes) cleanup to aesthetic impact limits may be appropriate.

6.2.7 Soil Leachate Methods

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The Storage Tank Di[illegible]ching Procedure (TCLP) as an acceptable leaching p[illegible] contaminants on groundwater. The department has a[illegible]ulate conditions at the site. Acceptable alternative leaching procedures, with their associated petroleum hydrocarbon parameters, are listed in Table 3. Results of all leachate testing must be reported based on the concentration in the leachate (μg/l or mg/l).

7.0 SAMPLE HANDLING, PRESERVATION, AND HOLDING TIME

To draw valid conclusions from sampling data, sample locations must adequately represent the source, samples must be properly collected, placed in proper containers, properly held and/or preserved until transport to the laboratory, and properly analyzed at the laboratory. Improper technique during any of these steps may lead to invalid data and invalid conclusions at the site.

Samples collected at petroleum hydrocarbon release sites must be handled in a manner that is consistent with the analytical testing that will be performed and that preserves the integrity of the samples. Samples must be handled in a manner that minimizes loss of organic contaminants due to volatilization or biodegradation.

Table 4 lists sample container requirements, preservation procedures, and maximum recommended holding times for parameters measured at petroleum hydrocarbon release sites. The purpose of preservation procedures is to minimize changes in samples from the time of sample collection until lab analysis. Preserved samples do not “keep” indefinitely. Preservation extends the useful life of the sample, but in order for the sample constituents to adequately represent the sampled source, the sample must be analyzed within a specific time period known as the “holding time”.

7.1 Sample Holding Time

Sample holding times for methods with multiple analytes are designed to protect the most easily degraded analytes. Some analytes are rapidly lost when not properly handled or preserved, while other analytes will remain in the sample beyond the recommended sample holding time for long periods of time even when not properly preserved.

When holding time is exceeded before analysis, the usability of the “compromised data” depends on its use and specifically on such factors as the relationship between sample levels and target RBSLs, the type of decisions to be based on the data, the presence of other data from other samples, stability of the analytes, and other factors. Results from samples analyzed past holding times are not necessarily worthless. Metals and persistent organic contaminants, such as PCBs, have been in the environment for years. Loss of metals and persistent organic contaminants within sample containers are not likely to be significant. Moreover, high concentrations of contaminants may be toxic to microbes and therefore self-preserving. Additionally, when sample holding times are exceeded, it can be assumed that results from such problem samples represent minimum values and are useful as minimum values, such as when minimum values exceed RBSLs. Soil samples for VOC analyses should be laboratory analyzed within the 14 day recommended holding.

Reported analytical results must include the sampling date and the date the samples were extracted and analyzed. In addition, the lab must qualify all results analyzed past holding times and all results from improperly preserved samples or from samples in improper sampling containers.

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7.2 Groundwater Sa

Groundwater is sampled for any of the following reasons:

- to define the horizontal and vertical extent of contamination;
- to monitor changes in concentrations of contamination;

- to document movement of contaminant plumes; and/or

- to determine background groundwater quality.

In all cases, a groundwater sample should be representative of the formation in which the well is screened. Various sampling devices and methods have been developed to achieve this objective.

The following items should be considered, independent of the sampling method used:

- The standing water within the well casing and screened interval may not be representative of actual aquifer conditions due to volatilization and the adsorption/desorption of contaminants from the well casing and screen materials. Traditionally, the standing water has been purged from the well before a sample is collected or the standing water above the well screen has been isolated by inflating a packer (in which case the water within the screened interval and in the filter pack material surrounding the well screen is still purged). A frequently used guide to determine how much water should be removed is to remove three to five borehole volumes (the volume of water in the well casing and screen plus the water in the filter pack) before samples are collected. More recently, low-flow (or micropurge) sampling techniques have been developed to purge water from within the screened interval at a low flow rate (e.g., $\leq$ 1 liter per minute) until indicator parameters (e.g., dissolved oxygen, DO, temperature, specific conductance, pH) have stabilized. The low-flow sampling techniques not only obtain more representative groundwater samples, they also significantly reduce the volume of purge water.

- Some wells will purge dry before the indicator parameters have stabilized or before three to five borehole volumes have been removed. When this occurs, samples should be obtained when the well has recharged sufficiently to allow sample collection.

- If three to five borehole volumes are being purged, remove the standing water beginning at the top of the water column (or immediately below the packer). If low-flow sampling techniques are being used, make sure that the purging/sampling device is located in the middle of the screened interval.

- The volume of purge water, the indicator parameter readings (e.g., pH, temperature, DO, specific conductance) and changes in the water turbidity should be documented in the field sampling notes, along with the presence of any odors or sheen.

- Minimize sample agitation and atmospheric contact as much as possible to minimize volatilization of contaminants and changes in the water chemistry.

- Decontaminate all purging and sampling equipment before and after inserting the equipment into the well to avoid cross-contamination between sampling locations.

- Indicator param RESCINDED should be taken in separate containers from

- Use the appropriate sample containers and preservatives for the parameters being analyzed. See Table 4 for a listing of the appropriate sample containers and preservatives.

- Groundwater samples for analysis of volatile components should be collected in a manner that minimizes loss of dissolved volatile components. Suction lift pumps should never be used to collect samples for volatile organic analysis since reducing the pressure over the sample may cause volatile constituents to come out of solution.

7.3 Field Filtration

In general, the purpose of sampling groundwater is to determine the concentrations of contaminants that are capable of migrating in the groundwater. Monitoring wells installed in some formations will yield high levels of suspended particulate materials. This suspended sediment contains naturally occurring heavy metals and other organic compounds that preferentially adsorb onto the suspended sediment. The degree of suspended sediment also depends on the degree of well development, the time intervals between well development and sampling, and the groundwater sampling method.

Heavy metals are the sample parameters that are most affected by the adsorption/desorption of contaminants from suspended sediment and by changes in the water chemistry. Samples being analyzed for concentrations of dissolved heavy metals should be filtered, which can remove most of the suspended sediment from the sample. Acid preservation can remobilize heavy metals and other contaminants from suspended sediment, potentially resulting in an overestimate of the contaminant concentrations. Therefore, the samples should not be preserved prior to filtration. Low-flow sampling techniques can reduce the turbidity of the sample, potentially avoiding the need for sample filtration.

While the DEQ guidance allows samples to be filtered by the laboratory within 24 hours of sample collection, field filtered samples are more representative because they have less chance to have the sample chemistry altered due to changes in pressure, pH and dissolved oxygen concentrations. Traditionally, 0.45 micron (μm) filters have been used for dissolved heavy metal samples. Five (5) μm filters may yield a more representative sample of the mobile contaminant fraction by including both dissolved metals and metals that are suspended on mobile colloids. In-line cartridge filters are preferred since the exposure of the sample to changes in pressure and dissolved oxygen concentrations is minimized.

Groundwater samples for volatile organic analyses should not be filtered to remove suspended particulates. Suspended particulates do not interfere with volatile organic analysis and vacuum filtration strips volatile contaminants from solution. Groundwater samples for analyses for PNAs or DROs should not be filtered since these compounds may be absorbed on paper filters. If there is a desire to remove particulates from groundwater samples to be analyzed for these parameters, the particulates should be removed by either settling or centrifuging.

7.4 Soil Sampling Considerations

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Soil samples are collected to determine the horizontal and vertical extent of contamination and to identify subsurface conditions that a[illegible]quently, the corrective actions to address the contaminatio[illegible]ample is one which has been changed as little as possible[illegible]nt.

The soil sampling procedure to be utilized for volatile organic compounds (VOCs), e.g., BTEX, sediment sampling is EPA SW-846, Method 5035, Soil Sample Collection and Methanol Preservation for VOAs. This procedure is intended to minimize loss of organic contaminants due to volatilization and/or biodegradation. Appropriate sampling devices must be capable of rapidly collecting samples with a minimum of atmospheric exposure. All soil samples for laboratory analysis should be collected from a freshly exposed surface. Exact field measurements of the sediment sample and the methanol preservative are required to ensure accurate laboratory analytical results. Soil Sampling utilizing Method 5035 is required for the analysis of all soil samples at sites.

Collecting duplicate samples in case of breakage or for leachate an analysis is recommended. These samples need to be extracted and analyzed within the original sample holding time. Field screening should be performed on split samples in separate containers (preferably widemouth jars), not in the containers selected for laboratory analysis. Once the samples have been placed in the sample containers, the sample containers should not be reopened until they arrive at the laboratory. All samples must be cooled to 4°C immediately after collection and kept on ice until arrival at the laboratory.

The GRO method provides sampling and preservation procedures using either methanol preservation/extraction procedures or soil as collected without methanol preservation. Either technique may be used, provided that the applicable RBSLs are within the detection levels. Methanol preservation is superior to unpreserved soils and is preferred.

7.5 Contamination

To avoid cross contamination of samples, petroleum products should not be handled prior to sample collection. If it is necessary to handle petroleum products prior to collecting samples, then steps must be taken to avoid sample contamination such as washing hands after refueling your vehicle. Tank removers doubling as samplers should wear protective coveralls during tank removal and take them off before sampling. Vehicle exhaust and ambient gasoline vapors are another potential source of contamination. Do not store samples in the same location with fuel, such as with a gasoline container in the back of a truck or car trunk. Use of sample blanks to measure potential sources of contamination is discussed in Section 8.

Any sampling equipment that comes in contact with the sample should be thoroughly cleaned to remove any remaining residue before additional samples are collected. The cleaning procedure depends on the type and amount of contamination remaining on the sampler. For low level contamination, steam cleaning or cleaning with trisodium phosphate or other detergent followed by triple rinses with contaminant free deionized water should be adequate. However, where high concentrations or free product are involved and especially for those products that are only slightly water soluble, suitable solvents such as methanol or acetone should be used or the sampling equipment should be discarded. The adequacy of equipment cleaning procedures should always be evaluated through the use of blanks.

7.6 Chain of Custody

Evidence in the form of sample analytical results is used to document site investigations. A consultant submitting analytical documentation must provide a chain of custody record. Therefore, it is imperative that chain of custody procedures be followed whenever samples are collected, transferred, stored, analyzed, or destroyed. [...]s is to create an accurate written record which ca[...] RESCINDED [...]f samples from the time of sample collection throu[...]

A sample is in custody if it is in actual physical possession, is in view, is in locked storage, or is kept in a secured storage area restricted to authorized personnel. All samples collected should be maintained in custody with the chain of custody record during transportation to the laboratory. Whenever samples cannot be maintained in physical possession, whether in the field or laboratory, the samples must be either locked inside vehicles or placed in a secure sample storage area.

The sample collector should complete Chain of custody records when samples are collected and should be signed or initialed with dates and times. Chain of custody records should include the following:

- Project name
- Sample identification number
- Sample date
- Sample time
- Sample location
- Number of containers per sample location
- Type of preservation
- Analysis requested
- Name of the collector
- Pertinent field data
- Other remarks or comments

When transferring possession of the samples to the laboratory, the sample custodian will sign the chain of custody record and assume custody. The time, date, and the custodian's signature must appear on the chain of custody record.

When an intermediate is required to deliver samples to the laboratory, the intermediate must assume custody of the samples. The identification tag, if required, and chain of custody record must contain their signature with the date and time custody of the samples was assumed.

After arrival at the laboratory, each sample should be assigned a unique number by the laboratory custodian. This number should also be recorded into a permanent laboratory log book. The laboratory custodian will also record the person delivering the sample, the person receiving the sample, date and time received, source of samples, condition of the samples, and any other pertinent information.

The samples must be stored, at the proper temperature, in a secured storage area until analyses.

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8.0 QUALITY CONTROL

Any party generating data has the responsibility to implement minimum procedures to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented.

The quality of data from a site sample analyzed in a laboratory can be no better than the sample. When a sample is collected with improper procedures, or with improper preservation, the results from that sample may be compromised. Consequently, procedures must be in place to assure that site samples are the highest quality possible. Field procedures which might impact the integrity of samples include sampling procedures, sample handling and preservation procedures, decontamination procedures, and field quality control procedures.

8.1 Field Quality Control

An integral part of any quality assurance program includes field QC samples. Blank, split and replicate samples are common types of field quality control samples useful for evaluating sources of errors. These are particularly valuable for evaluating the effectiveness of sampling strategies and estimating the precision and accuracy of results. Field QC samples should be handled and stored in an identical manner as the actual samples.

8.1.1 Blanks

In general, blanks are sample containers filled with reagent water (water free of the analytes of interest) or rinse water and used to check possible sources of contamination. Three different types of blanks are described below.

8.1.1.1 Field Blanks

A field blank is a sample container filled with reagent water, and preservatives as appropriate in the field as a check on possible container contamination, preservative contamination, or reagent water contamination. Field blanks are required for all water samples at a frequency of one blank per batch or 20 samples, whichever is less.

8.1.1.2 Trip Blanks

A trip blank is a special type of field blank, filled and capped in the lab, and sent to the field with other sample containers. The sample remains unopened in the field, is stored with other site samples, and is returned to the lab where it is analyzed as a check on possible container contaminants and possible diffusion of contaminants between samples. Trip blanks are only used for volatile organic samples.
No frequency guidelines are presented for trip blanks, since field blanks also measure this contaminant source.

8.1.1.3 Sampler and Equipment Blanks

Bailers or pumps are frequently used and reused in monitoring wells to collect samples and must be cleaned between each use. After cleaning, the sampler is rinsed again with contaminant free water and this final rinse water is sampled to determine if contaminants persist on the sampler after cleaning. Trihalomethanes (chloroform, bromoform, chlorodibromomethane, and bromodichloromethane) are common contaminants of field blanks. These compounds originate from chlorinated municipal water or bottled water purchased at retail outlets used to clean sampling equipment.

Chlorinated water should not be used to clean sampling equipment when associated samples will be analyzed for volatile halocarbons. Sampler blanks are also important wherever samplers are reused between two or more sample locations for the collection of water samples. The frequency of sampler and equipment blanks depend on the type of contaminant, contaminant levels, sampling procedures, and equipment cleaning procedures.

In addition, vacuum filtration units are used on site to filter groundwater samples for dissolved metals analysis. The filtration apparatus should be cleaned between each sample, assembled with filter pad, prefilter, and filter, (as appropriate) and then a sample volume of reagent water is run through the cleaned filtration unit, as a filtration blank, to check possible contamination remaining on the unit.

The minimum frequency for sample blanks is one per batch of samples or per 20 samples, which ever is less. The frequency of sampler blanks should be increased when high concentrations of contaminants are common, and when false positives cannot be tolerated.

Results of field, trip, and sampler blanks must be included in the remedial investigation and the closure reports. Positive results from blanks identify and quantify contamination which could be present in other samples in the sample batch. Positive blank results may also indicate that equipment cleaning procedures need to be changed or modified. Sample results should never be corrected by subtraction of blank results. Blank values are an indication that samples may be contaminated with the same compounds at similar levels and ranging up to 2 to 3 times the levels of the blanks.

8.1.2 Split Samples

Split samples are two or more separate samples from the same source collected at the same time, and sent to two or more different labs as an overall check on field and lab sources of error. Results must be evaluated by taking into consideration the acceptance "windows" of the two labs, plus sampling error, and allowances for heterogeneous matrices (soils and solids). If the two labs produce results which differ by more than might be anticipated from random error, confirm that the samples are genuinely split samples and that the same methods were used, then have the labs re-evaluate their calibration and batch quality control information. If there is still no explanation for the differences it may be useful for the two labs to exchange calibration standards or repeat analysis of another split sample set.

8.1.3 Field Replicate S

Field replicates are duplicate samples taken from the same source at the same time. The difference between replicates is a measure of sampling and analytical variability (error) and the non-homogeneity of the sampled source. Field replicates are an indication of the amount of variability that can be expected between samples in the absence of real changes in analyte concentration.

8.2 Laboratory Selection Criteria

The first step toward assuring the accuracy of lab data for a project is to select a laboratory that can demonstrate acceptable performance for the parameters of interest. The ability to produce acceptable data should be reviewed by someone with experience and should consist of a thorough review of the labs standard operating procedures (SOPs), and method performance.

8.2.1 Standard Operating Procedures (SOPs)

A commercial laboratory with the ability to perform the necessary range of analytical services for investigation of LUST releases in Michigan should have well developed SOPs for measurement of VOCs, PNA compounds, PCBs, cadmium, chromium, and lead in both soil and water samples. The SOPs should include:

- descriptions of instruments, equipment and reagents used in the method.
- step by step procedures covering all steps in the calibration and maintenance of the instrument and analysis of samples.
- all quality control samples with corresponding compounds, levels, frequencies, acceptance windows and procedures followed by the analyst and lab when audits are outside of acceptance windows.
- summaries of performance information for QC standard and sample spikes.
- data and calculations used to determine detection levels.

8.2.2 Performance Evaluation Study Results

The lab should also be able to provide results of USEPA Performance Evaluation samples or independent suppliers of performance evaluation samples.

8.2.3 Lab Certification

Some labs will also be able to show certifications from other states or independent certification agencies for the specific parameters of interest to the project. Michigan does not currently have a laboratory certification program for environmental laboratories. The Michigan Department of Environmental Quality administers a certification program under the Safe Drinking Water Act. Certification under this program for volatile organi[...] hese parameters in water samples. Further informati[...] gram is available from the Michigan Department of E[...] gical Protection Division.

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The USEPA, Office of Pollution Prevention and Toxics administers a voluntary lab accreditation program for labs involved in the analysis of lead in paint, dust, and soil.

8.2.4 Other Lab Selection Criteria

In addition to having the appropriate capability and acceptable performance, other important selection criteria include price schedules (including availability of volume discounts), ability to meet project turn around times, equipment and instrumentation including redundancy or backup in the event of equipment problems, qualified and experienced staff, and experience with similar projects.

8.3 Laboratory Quality Control

The responsibility for conducting a valid investigation and completing an appropriate site closure rests with the consultant or project manager and ultimately with the responsible party. The validity of the investigation hinges on having data of known and acceptable quality. Data should be evaluated periodically throughout the course of the investigation and cleanup to assure validity. In addition, data should be evaluated whenever the need to review data is suggested by inconsistent split sample data, suspected contamination or carry over, poor agreement between field and lab data, unusual data, apparent outliers or data which is otherwise inconsistent with other existing site data.

8.3.1 Initial Demonstration of Performance

The laboratory must make an initial demonstration of the ability to achieve acceptable accuracy, precision, and detection levels with each new method or method modification by successful analysis of replicate samples as described below. This information should be included in each SOP.

8.3.1.1 Replicate Water Sample Spikes

Analyze at least four replicates (four samples) of a QC check sample containing each analyte of interest at a concentration at or below five times the laboratory method detection level. Calculate the average recovery and the standard deviation for each analyte of interest using four or more results. All recoveries must be between 70% and 130% (unless another method performance recovery is specified in the method for spikes). In all cases, recoveries must be greater than 50% and concentration of the four samples must not vary from the mean by more than 20%. If the percent relative standard deviation or percent recovery for any analyte is exceeded, then system performance is unacceptable for that analyte. This evaluation must be repeated each time there is a significant change in the method.

Note: If the MDL is determined with the same spike level as required by this section (or lower), with acceptable performance as specified in this section, then the MDL determination can be substituted for the requirements of this section.

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8.3.1.2 Replicate Soil Sample Spikes

Analyze at least four replicates (four samples) of a fortified soil matrix containing each analyte of interest at a concentration between three and five times the laboratory MDL. Calculate the average recovery and the standard deviation for each analyte of interest using four or more results. All recoveries must be between 70 and 130% (unless another method performance recovery is specified in the method for sample spikes). In all cases recoveries must be greater than 50% and the concentration of the four individual measurements must not vary from the mean by more than 20%. If the percent relative standard deviation or percent recovery for any analyte is exceeded, then system performance is unacceptable for that analyte.

8.3.2 Determination of Method Detection Limits

The laboratory must determine the method detection limit (MDL) as specified in 40 CFR, Appendix B for all compounds and elements used in the evaluation of releases. The MDL determination should be run on reagent water. The MDLs must be at or below those target MDLs identified in Op-Memo #4.

8.3.3 On-going Quality Control

Analytical quality control procedures include the routine use of method blanks as a check on contamination, calibration checks or control samples (preferably at two concentrations) to verify calibration in each run, the use of sample spikes and duplicates to verify sample recovery and reproducibility, and surrogate spikes in every sample to verify the entire analytical procedure from preparation through analysis.

With every batch (a group of samples analyzed sequentially) of 20 or fewer samples analyzed, the lab must also analyze certain quality control samples, and meet specific performance requirements as outlined below:

8.3.3.1 Method Blank

A method blank must be analyzed with every batch of samples. All target analytes must be below Method Detection Limits. When detection limits are exceeded in the method blank, sample analysis should be discontinued until contamination is brought back into control. Affected samples should be qualified or reanalyzed. Method blank results (including surrogate spike results for the method blank) must be reported with their associated sample results.

8.3.3.2 Matrix Spike Duplicates

A matrix spike and its duplicate must be analyzed in every batch of samples. The spike concentration should fall in the upper half of the calibration range. The spike recovery should be between 60 and 140% unless another method performance recovery is specified in the method. In all cases, recoveries must be greater than 50%.

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8.3.3.3 Surrogate Spikes

Surrogate spikes must be analyzed with every organic analysis; the surrogate data must be submitted with each sample; and the surrogate data must be within the appropriate windows (identified below). In those cases where the acceptance window is not met, and the problem cannot be attributed to a correctable cause, the sample must be reanalyzed. If the surrogate(s) sample is still not within the acceptance window in the repeat analysis, the sample results must be reported with a qualifying statement explaining the sample matrix or analytical problems and providing guidance concerning the usability of the sample results.

Surrogate Compounds[1]	Spike (µg/l)	Water % Rec.	Spike (mg/kg)	Soil % Rec.
Volatiles by GC				
a,a,a-Trifluorotoluene	20	75-125	20	50-150
Volatiles by GC/MS				
Toluene-d8	20	88-110	20	84-138
Bromofluorobenzene	20	86-115	20	59-113
1,2-Dichloroethane-d4	20	76-114	20	70-121
PNAs by HPLC				
Decafluorobiphenyl	100	40-120	1000	30-150
PNAs by GC/MS				
Nitrobenzene-d5	100	34-114	1000	23-120
2-Fluorobiphenyl	100	43-116	1000	30-115
p-Terphenyl-d14	100	33-141	1000	18-137

[1]Alternative surrogate compounds may be used which encompass the range of the temperature program used in the method.

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9.0 LABORATORY DOCUMENTATION AND REPORTING

9.1 Content of Lab Reports

Laboratory results submitted to support closure must be submitted on the original laboratory data sheets. This data may also be tabulated, summarized, and presented in other formats to meet the needs of the project report. The original laboratory data reports must include the following information:

- Sample Field ID.
- Laboratory sample identification numbers and corresponding field sample identification numbers.
- Method of analysis as specified in this guidance, e.g., Method 8021 or Method 8310. If methods other than those specified in this guidance are used, the complete method number, title, and source must be identified.
- Obvious sample odor must be reported. Consultants or lab analysts are not encouraged to sniff samples. However, sample odor must be reported if it is obvious in handling the sample. Odors should be reported in the comment field or section of the lab report.
- Specific parameter or analyte(s).
- Report soil results as ug/kg on a dry-weight basis. Report groundwater results in ug/l.
- Report the percent moisture of soil samples.
- Report the dilution factor for samples or extracts that required dilution to bring the sample concentration within the analytical range of the method.
- Report the lab MDL or TMDL (Op-Memo #4) used to report data for the specific method or analyte.
- Date sample was collected.
- Date sample was extracted.
- Date sample was analyzed.
- Report the pH of preserved water samples submitted for analyses of BTEX compounds, volatile halocarbons, GRO, DRO, lead, cadmium, and chromium. The pH of volatile samples may be determined after sample analysis has been done so as not to compromise the sample.
- Questionable data should be flagged. Examples of questionable data include exceedance of sample holding times; failure to meet QC requirements; instrument failure during analysis; improper sample preservation; or any other relevant factors.
- Report the presence of unknown or non-target peaks in the comment section of the lab report when such peaks appear on the sample chromatogram. Examples of this are: 1) a peak on a GC chromatograph for which no standard has been run; 2) diesel peaks tailing the end of a gasoline range chromatograph.

- Analyst’s signature (or the signature of the analyst’s supervisor or QC manager.)
- QC data associated with the sample result. With every batch of 20 samples or less the results of either: 1) two replicate spikes (accuracy and precision); 2) one matrix spike; or 3) surrogate spikes. These results must be reported as percent relative standard deviation or percent recovery as appropriate.
- Labs should have Standard Operating Procedures for all methods and procedures. Any deviations from laboratory SOPs must be reported in the comment section of the lab report.
- All records including original data and chromatograms, must be kept a minimum of three years.

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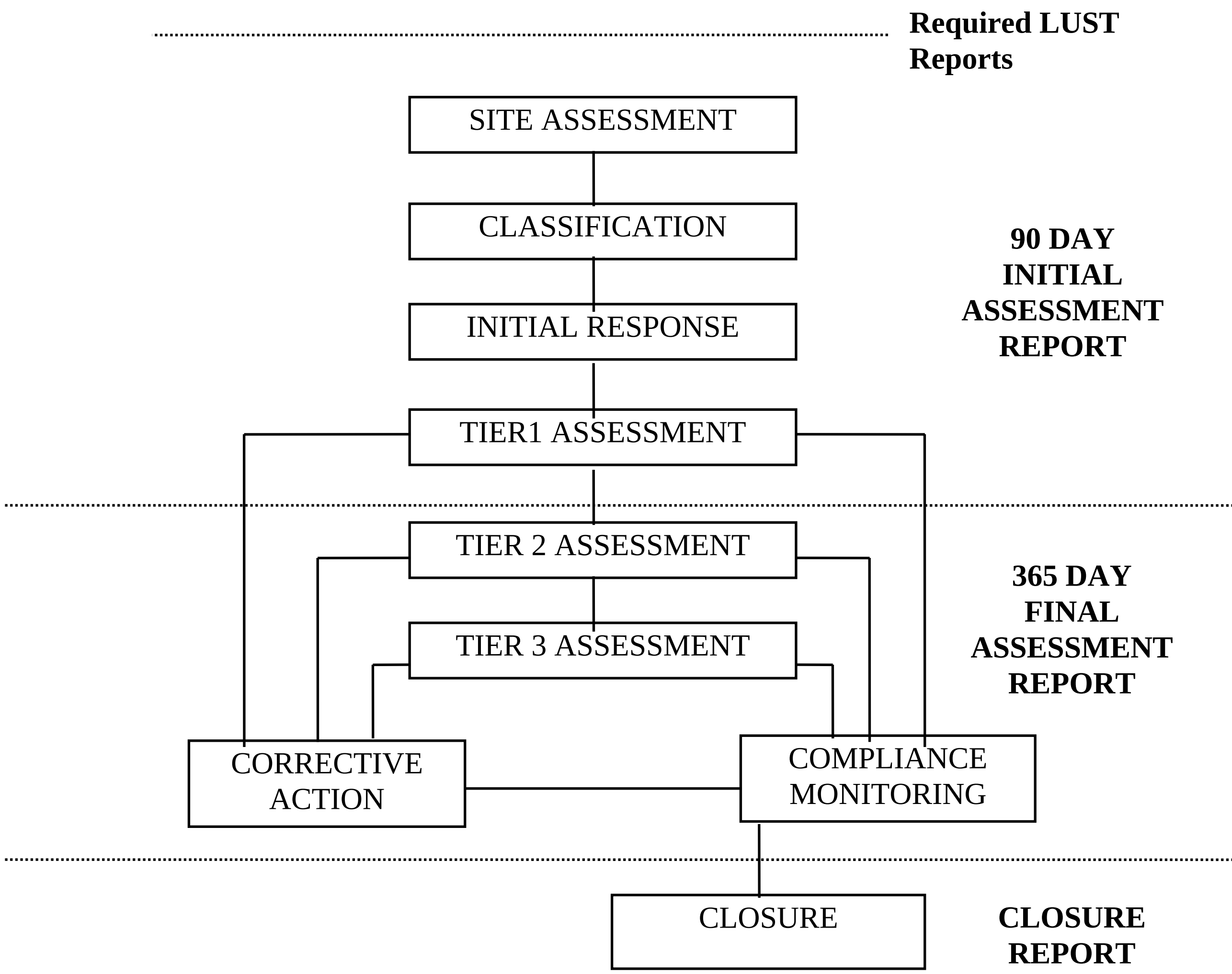
10. RISK-BASED CORRECTIVE ACTION OVERVIEW

10.1 Introduction to Risk-Based Corrective Action

Risk-Based Corrective Action (RBCA) is a decision-making process that allows a Qualified Consultant (QC) who has been retained by an owner/operator to assess and respond to hydrocarbon releases. Sites vary in complexity, physical and chemical characteristics, and risks they pose to human health and the environment. The RBCA process allows QCs and regulators to take a flexible tailored approach to assessing and remediating sites; this approach can be more cost-effective than traditional approaches. Figure 1 is a simplified flow chart, illustrating the RBCA process and the reporting requirements under Part 213.

Figure 1. LUST/RBCA FLOW CHART



A Michigan Specific approach was used to take into account relevant Part 213 requirements for the utilization of the American Society of Testing and Materials (ASTM) Standard Guide for Risk-Based Corrective Action (RBCA), E 1739-95, which is adopted by reference in Part 213. Several policy decisions were make to customize the RBCA process into a Michigan specific process.

One of the key policy issues which apply to all sites as part of a RBCA analysis, is that groundwater in Michigan is protected for all uses, and thus is considered the receptor at all locations, unless the site groundwater is reliably restricted or the groundwater, do to insufficient quantities and isolation, can be eliminated as a pathway of concern.

The Storage Tank Division (STD) has issued several operational memoranda, including the Tier 1 Risk-Based Screening Levels (RBSLs) lookup tables, to provide guidance on all reasonable and relevant exposure assumptions and pathways in establishing cleanup criteria for corrective action activities undertaken under Part 213. Please refer to these documents as needed to assist in implementing corrective action activities. Most, if not all, operational memoranda will be available on the STD internet homepage (http://www.deq.state.mi.us/std/).

A generic outline of the RBCA process follows as the remainder of this section.

The RBCA process allows users to:

- base decisions on reducing to appropriate levels the risk of harmful human or environmental impacts

- focus site assessment activities on collecting information to make risk-based corrective action decisions

- focus limited resources toward sites that pose the greatest risk

- find the most economical remedial option "that has a high probability of achieving the negotiated degree of exposure and risk reduction"

- evaluate compliance "relative to site-specific standards applied at site-specific points of compliance"

RBCA integrates risk and exposure assessment practices. The process uses a tiered approach that consists of:

- *tier 1*, the preliminary site assessment and establishing risk-based screening levels

- *tier 2*, site-specific target levels and points of compliance

- *tier 3*, site-specific target levels and points of compliance

After the user completes a tier, he/she decides if more site-specific analysis is required.

Transition between tiers 1 and 2, or further tier analysis, must be evaluated by answering the following questions:

- Are conditions at the site similar to the generic assumptions used to calculate tier 1 RBSLs? If conditions are similar, then further analysis is probably unwarranted since it is likely to yield a similar target level for concentration reductions at the site.

- Will tier 2 site-specific target levels (SSTLs) differ significantly from tier 1 RBSLs? If site conditions are significantly different from generic assumptions, tier 2 analysis will probably yield SSTLs for the site that differ significantly from RBSLs. These SSTLs may be higher or lower than RBSLs determined in tier 1.

- Is the cost of remediation to tier 1 RBSLs less than or equal to further tier analysis? This is a simple cost-benefit analysis of the option of performing further tier analysis.

The RBCA process encourages application of corrective actions activities at appropriate receptor points or points of compliance, as a result of potential/viable migration pathways, rather than an arbitrary boundary. This application may, however, also require notification to off-site property owners or the use of institutional controls depending on the site specific conditions.

10.2 Tier 1

The tier 1 analysis enables the user to classify the site and decide how urgently sites require initial corrective action. Individuals obtain information from:

- historical records

- visual inspection

- minimal site assessment data

Tier 1 consists of:

- the initial site assessment

- site classification and initial response

- comparison of site conditions with tier 1 RBSLs and tier 1 corrective action selection; to reduce the computational burden, look-up tables with RBSLs are available

10.2.1 *Tier 1, Step 1: Initial Site Assessment*

The user gathers site assessment data on:

- source characterization

- potential for exposure and degradation of beneficial uses

- extent of migration

Source characterization. Individuals use historical records to identify site activities and past releases and locate major sources areas. The site assessment is designed toward:

- identifying contaminants of concern and major contaminant sources

- identifying maximum concentrations of the most prevalent toxic and mobile compounds

- identifying if soil and groundwater are impacted

- sampling all media soil, groundwater, and soil gases, if appropriate.

Potential for exposure and degradation of beneficial uses. This includes gathering data from visual inspections, well inventory records, engineering drawings and hydrogeological assessment data to:

- locate human and environmental resources that could be potential impacted receptors

- identify potential significant transport and exposure pathways (groundwater transport, vapor migration through soils and utilities)

- identify current and potential uses of the land, groundwater, surface water and sensitive habitats

Extent of migration. Individuals need to sample not only source areas but also potential points of exposure or concern. If concentrations exceed the tier 1 RBSLs, or other criteria, the sampling should also identify potential preferential migration pathways.

Finally to expedite the review process, users need to summarize data clearly and concisely in tables and figures.

10.2.2 *Tier 1, Step 2: Site Classification and Initial Response, Source Characterization*

Next, the user decides which classification scenarios fit the site. The scenarios, based on their threat to human health, safety or sensitive environmental receptors, include the general categories of:

- immediate threat = Class 1 site

- short-term threat (0 to 2 years) = Class 2 site

- long-term threat (>2 years) = Class 3 site

- no demonstrative long-term threat = Class 4 site

Operational Memorandum No. 5 provides further details on the classification criteria and initial response actions For instance, initial response actions may not require active remediation. The prescribed initial response actions may include conservative corrective action goals based on:

- RBSLs
- aesthetic criteria
- other appropriate standards such as maximum contaminant levels (MCLs)

Initial response actions can consist of:

- monitoring
- further site assessment

At all times, the user should reevaluate site classification when more data become available or if conditions change.

Determining whether groundwater has been impacted by a petroleum release consists of:

Groundwater contamination has been detected at numerous leaking underground storage tank sites where the unsaturated soils are not contaminated above the tier 1 soil leaching to groundwater exposure pathway RBSLs. When permeable soil types are present at a facility, leaching to groundwater is only one contaminant transport mechanism by which contaminants can migrate to the groundwater. Advection and/or bulk fluid flow allows contaminants to travel directly downward with little or no lateral migration or sorption to soils. In these instances, soil sampling may not detect product that migrated to the water table, unless the samples are collected in the exact area of contaminant migration. Therefore, additional assessment may be necessary to demonstrate that the groundwater has not been impacted by the release.

The owner/operator should conduct an investigation that will provide sufficient information to determine whether the groundwater has been impacted by a release. This could be accomplished by: collecting groundwater samples from the source area(s); demonstrating that a continuous, competent, confining layer is present, preventing the downward migration of contaminants to the groundwater; or providing site specific information regarding the soil types(s), the historical records concerning the releases(s), soil sample data and the depth to groundwater.

Collection of groundwater samples from beneath the source area(s) is the preferred method to determine if the groundwater is impacted by the release. If a groundwater sample is not collected, the QC should present his/her rationale for not collecting groundwater samples in the Initial Assessment Report (IAR), Final Assessment Report (FAR) and/or Closure Report. All appropriate documentation should also be included in these reports. The STD project managers and geologists may audit these reports. Therefore, it may be useful for the QC to contact the STD project manager prior to the submittal of the report to discuss his/her rationale for not sampling groundwater.

10.2.3 *Tier 1, Step 3: Comparison of Site Conditions*

The user now selects the "most reasonable potential exposure scenario" that fits the site. Receptors can include:

- residential areas
- commercial/industrial areas

- construction workers
- underground utilities
- sensitive habitats (i.e., wet lands, surface waters)

The user also needs to identify:

- primary sources
- secondary sources
- transport mechanisms
- exposure pathways

Next, for each compound and exposure pathway selected, the user can use the tier 1 RBSL look-up tables which are provided in Operational Memorandum No. 4 to identify the appropriate RBSL. The appropriate tier 1 screening level(s) can be based on:

- toxicity data for carcinogens and non-carcinogens
- aesthetic criteria
- ecological criteria
- background levels
- or other relevant criteria.

The RBSLs, are based on generic criteria established for each pathway. The toxicological information is generally obtained from the USEPA's integrated risk information system (IRIS) database, and health effects assessment summary tables (HEAST) or peer-reviewed sources. Hence the RBSL data is an "evergreen set of values" based upon the most current data available.

10.2.4 *Tier 1, Step 4: Evaluation of Tier 1 Results*

The user reviews the results of the tier 1 assessment and select one of four options:

- *No action*, if source concentrations do not exceed applicable screening level concentrations. Compliance monitoring may be implemented to ensure that conditions remain the same, or improve.
- *Final corrective action*, if source concentrations exceed applicable screening level concentrations.
- *Interim corrective action*, if achieving the necessary risk reduction is impractical due to technology or resource limitations. The responsible party may remove free product and/or treat hot spots, or areas of significant concern.

- *Tier upgrade-further analysis*, if other measures are impractical or inappropriate. The site may need to be reassessed. "This decision is typically based on comparing the cost of achieving tier 1 corrective action goals with the cost for tier 2 analyses, considering the probability that tier 2 site-specific goals will be significantly less costly to achieve than tier 1 goals." In moving to higher tiers, the "user is able to develop more cost-effective corrective action plans because the conservative assumptions of earlier tiers are replaced with more realistic site-specific assumptions."

If tier 1 corrective action goals are inappropriate, the user considers SSTLs and appropriate points of compliance. The SSTLs:

- are based on measured and predicted contaminant attenuation from the source areas

- rely on models that use predictive equations that are simplistic, and often algebraic or semi-analytical

- limit input to practically attainable site-specific data or easily estimated data

In most cases, if the tier 1 RBSLs cannot be achieved using site-specific data, the site will require institutional controls to reliably restrict the exposure to the contaminants, for current and future use of the site.

10.3 Tier 2

Tier 1 and tier 2 screening levels strive to achieve "similar levels of human health and environmental resource protection." At higher tiers the user can develop more cost-effective corrective action plans because the more realistic site-specific site assumptions replace the earlier conservative assumptions.

10.3.1 *Tier 2, Step 5: Expanded Site Assessment*

In tier 2:

- additional site assessment data may be required

- minimal incremental effort is required relative to tier 1
  only a limited number of pathways, exposure scenarios and chemicals are considered because many were eliminated during the tier 1 analysis

- goals are considered conservative

- goals are consistent with MDEQ policy and exposure criteria.

- the user establishes compliance points and target concentrations at these points

- the user uses assessment data and predictive modeling results to determine source area concentrations. Modeling may use actual site values such as infiltration rates, source sizes and aquifer modeling parameters

- tier 2 SSTLs may be derived from the same equations as RBSLs. RBSLs may be used at "reasonable points of compliance, points such as at property boundaries or negotiated compliance located somewhere between source areas and reasonable potential receptors ... corrective action goals for source areas are then based on demonstrated and predicted attenuation of compounds that migrate away from the source area."

10.3.2 *Tier 2, Step 6: Evaluation of Tier 2 Results*

After reviewing tier 2 analyses, the user selects one of four options:

- *No action*, if source concentrations do not exceed tier 2 SSTLs. Compliance monitoring may be implemented.
- *Final corrective action*, if source concentrations exceed tier 2 SSTLs; this may include source removal, treatment, containment technology and institutional controls
- *Interim corrective action*, if achieving the desired risk reduction is impractical due to technology or resource limitations. Interim corrective action may consist of treating hot spots, changing the site classification or reassessing the corrective action plan.
- *Tier upgrade*, which is "typically based on comparing the cost of achieving tier 2 corrective action goals with the cost for tier 3 analyses, considering the probability that tier 3 site-specific goals will be significantly less costly to achieve than tier 2 goals."

10.4 Tier 3

Tier 3 requires more refined data, and generally uses more sophisticated analysis techniques.

10.4.1 *Tier 3, Step 7: Expanded Site Assessment*

Tier 3 first uses more refined SSTLs. SSTLs are determined by:

- a more detailed site assessment, based on significant additional site data to refine site-specific parameters and improve model accuracy
- probabilistic evaluations using Monte Carlo simulations
- use of "numeric groundwater codes that predict a statistical distribution of exposures and risks for a given site"
- use of more sophisticated chemical/fate transport models

10.4.2 *Tier 3, Step 8: Evaluation of Tier 3 Results*

Again, the user selects one option:

- *No action*, if source concentrations do not exceed tier 3 SSTLs; but compliance monitoring may be required.
- *Final corrective action*, if source concentrations exceed tier 3 SSTLs. Corrective action may include source removal, treatment and containment technologies.

- *Interim corrective action,* if achieving the desired risk reduction is impractical. The user may address hot spots or other significant concerns, or reassess site classification and the corrective action plan.

10.4.3 ***Tier 3, Step 9: Implementing the Selected Corrective Action Program***
When everyone agrees that no further assessment is necessary or practical, the user needs to conduct an engineering feasibility study to confirm the most cost-effective option for achieving the final cleanup levels.

10.4.4 ***Tier 3, Step 10: Compliance Monitoring***

Compliance monitoring may be required to demonstrate the effectiveness of the corrective actions.

When RBCA goals have been achieved and compliance monitoring and site maintenance are no longer required, then no further action is necessary.

10.5 References

ASTM E 1739-95 “Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites”, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pennsylvania 19103; 215-299-5400.

Underground Tank Technology Update, “ASTM’s guide for risk-based corrective action”, University of Wisconsin-Madison, Department of Engineering Professional Development, 432 N. Lake St., Madison, Wisconsin 53706; 612-482-7945.

Table 1: Recommended Parameters for Common Petroleum Products

Parameters	Leaded Gasoline[1]	Unleaded Gasoline[2]	Petro. Solv[3]	Light Distillate Oils[4]	Residual Oils[5]	Used Motor Oils[6]	Waste Oils[7]	Unknown
BTEX	X	X	X	X		X	X	X
Trimethylbenzene Isomers (TMB)[8]	X	X	X	X	X	X	X	X
MTBE		X						X
1,2-Dibromoethane (ethylene dibromideEDB)[1]	X					X	X	X
1,2-Dichloroethane[1]	X					X	X	X
PNAs[9]			X	X	X	X	X	X
Naphthalene/ 2-methylnaphthalene	X	X						X
Cadmium[10]						X	X	X
Chromium[10]						X	X	X
Lead[10]	X					X	X	X
Volatile Halocarbons[11]						X	X	X
PCBs							X	X
Diesel Range Organics (DRO)[12,13]				X	X	X	X	X
Gasoline Range Organics (GRO)[12,13]			X					X

Footnotes:

1) 1,2-dichloroethane and 1,2-dibromoethane may be present in leaded gasoline and leaded aviation gasoline and should be analyzed for if believed to be present.
2) This category includes aviation gasoline, regular, mid-grade and premium unleaded fuels or any fuel blend containing MTBE.
3) Petroleum solvents include petroleum spirits, mineral spirits, VM and P naphthas and stoddard solvent.
4) Light distillate oils include fuel oils #1, #2, diesel oils #1-D, #2-D, kerosene, Jet A and jet propellants (JP) #4, #7 and #8.

5) Residual oils include residual fuel oils #4, #5 and #6 (Bunker C), lubricating oils and hydraulic fluids. Most of these fluids are mineral oil based and can be measured by methods identified above. However, some hydraulic fluids are synthetic or water based and will not be detected by these methods.
6) Used oil is any oil that has been refined from crude or synthetic oil and as a result of use becomes unsuitable for its original purpose due to loss of original properties, or presence of impurities. Used motor oils may be suitable for further use and may be economically recyclable. Used motor oils include spent motor oils, other lubricating oils and hydraulic oils from the servicing of automotive vehicles which are not contaminated by cleaning solvents or halogenated solvents.
7) Waste oil is defined as "used oil" that has been contaminated by spilling, or by mixing with other waste, hazardous or otherwise.
8) Trimethylbenzene isomers include 1,2,4- TMB and 1,3,5- TMB.
9) PNAs includes the 16 priority pollutant PNAs listed in Method 8310 plus 2-methylnaphthalene.
10) Metals measured in water are measured as dissolved metals.
11) Measurement of volatile halocarbons in used motor oil releases is not required if there is documentation that cleaning solvents and sources of volatile halocarbons have been excluded from used motor oil.
12) GRO (Gasoline Range Organics) and DRO (Diesel Range Organics) refer to methods referenced in Measurement of Hydrocarbons: Report on Activities to Develop a manual by the EPA UST Work Group, American Petroleum Institute, Midwest Research Institute, and Enseco Incorporated.
13) The GRO and DRO methods are used to address aesthetic cleanup concerns when target analytes are not present. At the present time the DEQ lab. is not doing GRO and DRO analysis.

Table 2: Acceptable Analytical Methods for Common Petroleum Products

Parameter	Water	Soil
BTEX & MTBE	8021, 8260	8021, 8260
trimethylbenzene isomers (TMB)	8021, 8260	8021, 8260
1,2-dibromoethane (ethylene dibromide - EDB)	8021, 8260	8260
1,2-dichloroethane	8021, 8260	8021, 8260
PNAs	8270, 8310	8270, 8310
naphthalene[1]	8260, 8270	8260, 8270
2-methylnaphthalene[2]	8270	8270
cadmium	6010, 6020, 7131	6010, 6020, 7131
chromium	6010, 6020, 7191	6010, 6020, 7191
lead	6010, 6020, 7421	6010, 6020, 7421
volatile halocarbons	8021, 8260	8021, 8260
PCBs	8082, 1656[3]	8082, 1656[3]
Gasoline Range Organics (GRO)	8015 Modified	8015 Modified
Diesel Range Organics (DRO)	8015 Modified	8015 Modified

Methods listed above are from EPA SW-846, **Test Methods for Evaluating Solid Waste**, unless otherwise noted. The most current version of each method listed shall be utilized.

1) Other acceptable methods, if laboratory capabilities allow, may include 8021, 8310, 8410 and 8275 (for soils)

2) Other acceptable methods, if laboratory capabilities allow, may include 8410, 8260, and 8310

3) Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater - The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater

Other methods may be used, however they shall be preapproved by the Storage Tank Division project manager.

Implementation of Method 5035 utilizing methanol preservation for the sampling of soil volatile organic compounds, as it applies to the leaking Underground Storage Tank program, will be announced at a future date.

Table 3: Acceptable Soil Leaching Procedures for Evaluating the Mobility of Specific Contaminants in Soil

Leaching Procedure	Leaching Fluid	Appropriate Parameters
EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) [1,2]	Buffered Acetic Acid pH: 2.88 or 4.93	Cd, Cr, Pb, PNAs, PCBs ZHE [3]: BTEX, MTBE, Method 8260 volatile organic compounds (VOCs)
EPA Method 1312 Synthetic Precipitation Leaching Procedure (SPLP) [1]	H_2SO_4 & HNO_3 @pH: 4.20 Reagent Water	Cd, Cr, Pb, PNAs, PCBs ZHE: BTEX, MTBE, Method 8260 volatile organic compounds (VOCs)
ASTM D3987-85 (ASTM Neutral) [1,4]	Reagent Water	PNAs, PCBs
ASTM D5233-92 (ASTM Single Batch) [1,2,5]	Buffered Acetic Acid pH: 2.8 or 4.93	Cd, Cr, Pb, PNAs, PCBs

Footnotes:

1) It is generally recommended, due to the spatial and temporal variations in contamination concentrations, to collect samples for both total and leachable contaminant concentrations to allow for a direct comparison between the two.
2) Sodium in the Method 1311 (TCLP) and the ASTM Single Batch extraction fluids may interfere with analysis of certain metals analyzed by graphite furnace procedures and thereby prevent attainment of the recommended method detection limits. To avoid interference from sodium, non-furnace analytical methods and/or a leachate procedure which does not contain sodium (e.g., Method 1312, SPLP) may be used.
3) ZHE: Zero Headspace Extraction is used for all volatile compounds.
4) The ASTM Neutral Leach Procedure provides for reporting the leachable contaminant levels in terms of the weight of the soil (mg/kg). However, in order to use this soil leaching procedure for the purposes of evaluating contaminant mobility and potential impact on groundwater, leachable contaminant levels must be reported in terms of the volume of the leaching fluid. This information must be conveyed to the lab prior to sample analysis.
5) This method is useful for large particle size materials. Any monolith subject to this method must also be evaluated with ASTM D4842-89 to evaluate freeze-thaw effects.

Table 4: Container, Preservation, and Holding Time Requirements for Common Petroleum Product Sampling and Analyses

Parameter	Matrix	Container[1]	Preservation	Maximum Holding Time
BTEX & MTBE	soil	wide mouth glass	MEOH, cool to 4°C	14 days
BTEX & MTBE[5]	water	glass	pH<2[2], cool to 4°C	14 days
Trimethylbenzene isomers (TMB)	soil	wide mouth glass	MEOH, cool to 4°C	14 days
Trimethylbenzene isomers (TMB)[5]	water	glass	pH<2[2], cool to 4°C	14 days
1,2-dibromoethane (ethylene dibromide - EDB)	soil	wide mouth glass	MEOH, cool to 4°C	14 days
1,2-dibromoethane (ethylene dibromide - EDB)[5]	water	glass	pH<2[2], cool to 4°C	14 days
1,2-dichloroethane	soil	wide mouth glass	MEOH, cool to 4°C	14 days
1,2-dichloroethane[5]	water	glass	pH<2[2], cool to 4°C	14 days
PNAs	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
PNAs	water	amber glass	cool to 4°C	7 days/40 days[6]
Naphthalene/2-methylnaphthalene	soil	wide mouth glass	MEOH, cool to 4°C	14 days/40 days[6]
Naphthalene/2-methylnaphthalene	water	amber glass	cool to 4°C	7 days/40 days[6]
Cadmium	soil	wide mouth glass	cool to 4°C	6 months
Cadmium	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Chromium[4]	soil	wide mouth glass	cool to 4°C	6 months
Chromium[4]	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Lead	soil	wide mouth glass	cool to 4°C	6 months
Lead	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Volatile halocarbons	soil	wide mouth glass	MEOH, cool to 4°C	14 days
Volatile halocarbons[5]	water	glass	pH<2[2], cool to 4°C	14 days
PCBs	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
PCBs	water	amber glass	cool to 4°C	7 days/40 days[6]
Gasoline Range Organics (GRO)	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
Gasoline Range Organics (GRO)	water	glass	pH<2[2], cool to 4°C	7 days/40 days[6]
Diesel Range Organics (DRO)	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
Diesel Range Organics (DRO)	water	glass	pH<2[2], cool to 4°C	7 days/40 days[6]

Containers, preservation and holding times are based on methods from EPA SW-846, **Test Methods for Evaluating Solid Waste**.

Footnotes on following page

Footnotes for Table 4:

1) Check specific method for appropriate container size. Glass screw-cap vials with Teflon lined silicone septa shall be used for liquid matrices. Wide mouth glass containers shall be capable of being hermetically sealed in the field and equipped with Teflon lined lids. Wide mouth glass containers shall be filled completely, and tapped slightly as they are filled to eliminate as much free air space as possible. A minimum of two vials should be filled per sample location.
2) Adjust to pH<2 with H_2SO_4, HCl or solid $NaHSO_4$.
3) Samples for dissolved metals must be filtered immediately on site before adding preservative or lab. filtered within 24 hours of collection and preserved immediately.
4) When analyzing for hexavalent chromium: aqueous samples shall be stored at 4°C±2°C and analyzed within 24 hours; soil samples shall be stored at 4°C±2°C, extracted within one month, and analyzed within four days after extraction.
5) Samples do not require acidic preservation if analyzed within seven days.
6) Aqueous samples shall be extracted within seven days and analyzed within 40 days after extraction. Soil samples shall be extracted within 14 days and analyzed within 40 days after extraction.

TABLE 5 Chemical and Physical Properties of Selected Organic Petroleum Constituents in Order of Increasing Molecular Weight.

Compound	Molecular Weight	Boiling Point (°C)	Water Solubility (ug/l)	Octanol/Water Partition Coeff. (K_{ow})
Benzene	78.11	80.1	1,800,000	135
MTBE	88.0	55	NA	NA
Toluene	92.14	110.6	530,000	620
1,2-Dichloroethane	98.98	83.47	8,500,000	30
Ethylbenzene	106.17	144.4	170,000	2,200
p-xylene	106.17	138	190,000	1,761
m-xylene	106.17	139	190,000	792
0-xylene	106.17	144.4	190,000	792
n-propylbenzene	120.9	159.2	NA	NA
1,2,4-trimethylbenzene	120.19	169.3	NA	NA
Naphthalene	128.17	218	31,000	1,950
Acenapthene	154.21	279	4,200	9,600
Acenapthylene	152.2	270	3,900	5,300
Fluorene	166.2	295	2,000	15,000
Anthracene	178.2	226.5	43	28,000
Phenanthrene	178.2	340	1,000	28,000
Ethylene Dibromide	187.86	132	4,200,000	86
Fluoranthene	202.26	375	210	79,000
Pyrene	202.3	393	140	80,000
Benzo(a)anthracene	228.29	415	9.4	410,000
Chrysene	228.3	448	2	410,000
Benzo(b)fluoranthene	252.3	unk.	1.5	1,150,000
Benzo(k)fluoranthene	252.3	480	0.8	1,150,000
Benzo(a)pyrene	252.3	495	1.6	1,150,000
Benzo(ghi)perylene	276.34		NA	3,200,000
Indeno (1,2,3-cd)Pyrene	276.3	530	0.022	3,200,000
Dibenzo(a,h)anthracene	278.3	sublimes	1	6,900,00
Tetraethyllead	323.45	200	NA	NA
Aroclor 1245	328.5		45	1,100,000